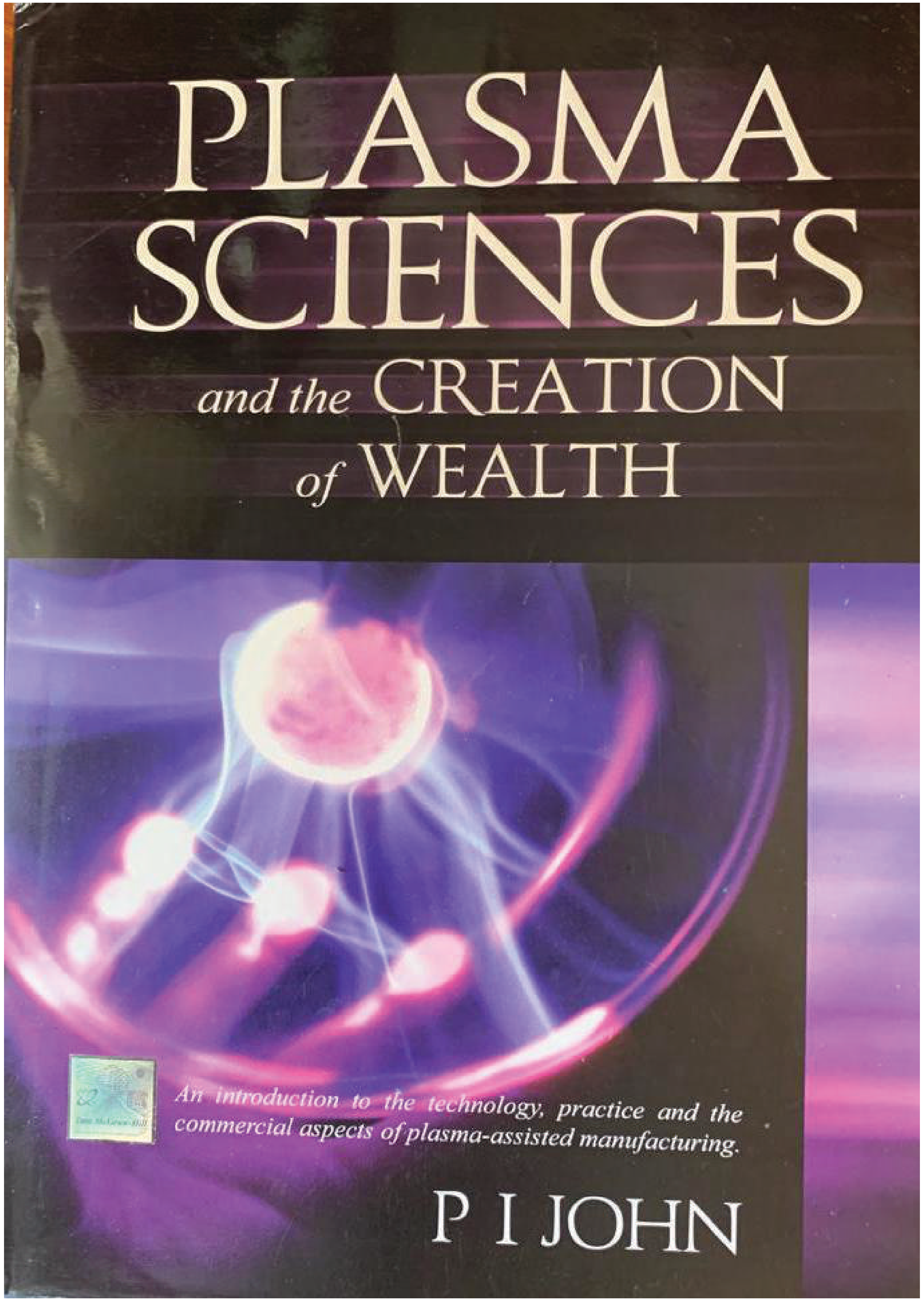

PLASMA SCIENCES
and the CREATION
of WEALTH

An introduction to the technology, practice and the commercial aspects of plasma-assisted manufacturing.

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Plasma Sciences and the Creation of Wealth

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About this Book

This book discusses the versatility of the plasma state of matter as an enabling tool for industrial, manufacturing, environmental and engineering applications. It is an introduction to the technology, practice and the commercial aspects of plasma-enabled material processing and manufacturing. The book is meant for the agents of change in the present-day society; students, entrepreneurs, businessmen, consultants and technocrats.

The introductory chapter discusses the linkages between science, technology and industrial development in a historical perspective. The newly emerging technologies, which will impact industry, manufacturing and lifestyles in the 21-st century are described briefly. The growth and development of plasma sciences and their contributions to fields such as thermonuclear fusion, space and astrophysical sciences are traced. A broad overview of the development of industrial applications based on plasma sciences is also given in this chapter.

Chapter 2 discusses the physics and chemistry of the Plasma State and describe its unique properties, which have the potential to germinate applications. Chapter 3 describes generic methods for producing plasmas in the laboratory, which forms the basis of industrial applications. Chapter 4 is devoted to the aspects of plasma as an industrial tool. This section describes how plasma state can generate extremely high temperatures, how plasma catalytic effects modify conventional chemistry and how powerful beams of charged particles and metal particle flux can be extracted from plasma sources.

Chapters 5-19 deal with specific applications in a variety of industrial areas. Each chapter is organised with an area of application as the focus. The applications cover a wide range: surface engineering of industrial and consumer products, plasma light sources and displays, environmental remediation, microelectronic and solar photovoltaic devices, waste destruction, metallurgy, recycling etc. The relevant processes and the plasma reactors are discussed in some detail. The applications are deliberately chosen from proven industrial situations with less importance given to basic studies related to applications. Consider the chapter on plasma nitriding: the scientific foundations of nitriding process and its modification in the presence of plasma is followed by a description of nitriding reactors and application of the nitriding process to a large variety of engineering components from knives to automobile components.

The last chapter on fusion deviates from the norm of discussing commercialised processes. However, I believe that its inclusion is justified because of the gigantic potential economic impact it would have once it is successful.

The approach justifies the title: the potential of the plasma technology to create wealth by adding value, reducing waste, improving environment and contributing to the quality of life.

1. The Age of Perpetual Innovation

Science, Technology and Industrial Revolutions

This chapter reviews the historical role of technology as the tool for creation of wealth and how industrial revolutions were driven by new technologies. Today's paradigm for knowledge-based manufacturing is based on a number of advanced technologies and incremental advancements. The science of the plasma state of matter has generated enabling technologies, which integrate the unique properties of the plasma state with processes relevant to industrial manufacturing and environmental remediation.

2. The Fourth State

Physics and Chemistry of Ionised Gases

Plasma is the ionised state of matter. This chapter discusses the fundamental properties of the plasma state of matter and describes some basic phenomena, which arise out of these. The fluids like properties of plasmas are derived from the long-range interaction between charged particles. Plasma chemical effects arise out of electron collision with neutral atoms and molecules. Plasmas interact with electric and magnetic fields and support flows, waves, self-organization and instabilities.

3. Taming the Lightning

Plasma Sources in the Laboratory

Plasma sources have evolved from the 19th century gas discharge apparatuses to the modern devices driven by the requirement for basic plasma research, fusion experiments and the need for industries to have reliable plasma processing systems. Plasma sources utilize ionisation by the impact of electrons energised by DC, RF and microwave electric field. The parameter space accessible to the modern plasma sources is quite extensive. In this chapter we will examine the various techniques for the production of plasmas in the laboratory.

4. Plasma as an Industrial Tool

Material Processing with Plasma

Interaction of plasma with solids and gases is the basis of plasma enabled material processing. The four foundations of plasma processing are the ability to produce energetic particles, sputtering process to generate metal atoms, chemical reactivity and the efficient conversion of electricity to heat. These, individually or in tandem can produce a number of effects, which have industrial applicability. This chapter discusses these aspects in some detail.

5. The Nitride Shield

Surface Alloying by Diffusion Treatments

When steel surfaces at elevated temperature are exposed to nitrogen plasma, the nitrogen atoms dissolve in the metal and form nitrides of the alloying elements. This is the plasma equivalent of a thermochemical diffusion process called nitriding. The Layer of surface nitrides form a hard shield against wear, corrosion etc. In this chapter, we shall discuss the plasma nitriding process and reactors and describe a variety of industrial products, which are benefited from nitriding.

6. Alchemy by Implantation

Surface Modification by Ion Implantation

Ions accelerated in plasma can be implanted into materials to modify their properties. Plasma ion implantation technique is less expensive compared to implantation using high-energy accelerators. The material properties can be changed to improve wear and corrosion resistance. Plasma implantation can also be used to assist other plasma based coating processes. A recently developed area of application is the doping of semiconductors.

7. Engineering the Tools

Surface Engineering by Functional Coatings

Wear of engineering tools and the friction caused by bad tools has both direct and indirect impact on manufacturing cost. Depositing hard coatings on the surface can decrease wear and increase tool life and performance. This chapter discusses various methods of plasma-based deposition of advanced coatings on engineering tools and describes the properties of coated products.

8. The Plasma Washing Machine

Precision Cleaning of Surfaces

Plasmas can clean surfaces by irradiation with energetic ions or by initiating chemical reactions by radicals. This technique is now finding increasing application for a variety of sophisticated industrial processes where extreme cleanliness of the surface is essential. Biological decontamination of surfaces and environment is also an emerging application. This chapter discusses the basic processes and applications to a few specific areas.

9. Biomaterials and Plasmas

Surface Modification of Polymeric materials

Materials used in biomedical applications have to be biocompatible and even bio-interactive. Various plasma techniques have been developed to render such properties to materials used in biomedical applications. This chapter will review these techniques and indicate applications, which have become important to modern medical practice.

10. Emperor's New Clothes

Plasma treatment of Textiles

Textile Manufacturing was one of the early industries, which formed part of the industrial revolution. Significant new developments are taking place in textile industry to meet the changing consumer tastes and increasing environmental pressures. Plasma processing has had a rebirth in the textile arena, with the earlier unsuccessful approach of using vacuum plasmas replaced by novel atmospheric pressure plasma. The process has ability to modify woven and non-woven textile surfaces to improve their properties. This chapter will discuss the role of plasma processing in textile industry

12. Harvesting the Sun

Plasma Processing for the Solar Economy

The major issues in solar energy technology are: conversion of sunlight into electricity or heat, storage of energy in portable devices and conservation of energy. Plasma processing has become an essential tool for a variety of devices required in all the three components of solar economy. This chapter describes plasma techniques for manufacturing amorphous silicon devices and sun control coating of window glass.

13. Inside Intel

Plasma in Microelectronic Device Processing

The convergence in information, communication and entertainment is a major outcome of the microelectronic revolution. The miniaturisation in electronic is made possible by the atomic scale manufacturing using plasma processing, which entered microelectronic manufacturing in the 1970's. This chapter explores the ways in which the core processes like etching, deposition and doping in microelectronics are enabled by plasma techniques.

14 Light Fantastic

Advanced Plasma Radiation Sources

Light emission in plasmas was one of the earliest plasma phenomena exploited for commercial applications. Excited atoms and molecules radiate light by a variety of phenomena. Starting with arc lamps and mercury vapour lamps, the technology has made immense progress over the years. Understanding the relevant plasma phenomena has aided in improving their efficiency and in tailoring the emitted light to mimic the natural light. This chapter examines the light emission phenomena in plasmas and the modern devices that commercially exploit them.

15. And Now on the Silver Screen

Plasma Techniques for Visual Displays

Giant screens with bright images are displacing the conventional television set in the living room. High definition displays using plasma panels is a major contender in the growing entertainment market. Plasma display panels use a programmable matrix of tiny plasma sources to display images. This chapter describes the basic properties of plasma display panels and their future.

16. Clearing the Air

Plasma Remediation of Air Pollution

Air pollution is a major problem accentuated by increasing urbanisation and industrialisation. The major sources of air pollution are automobiles, fossil-burning power stations and petrochemical industries. New techniques of using non-equilibrium plasma techniques to clean up emissions and improve the environment are described in this chapter.

17. Shiva's Third Eye

Plasma as the Ultimate Destroyer

Hazardous wastes are legacies of the second wave manufacturing. The intense heat in a plasma jet with temperatures exceeding 5000^o C can destroy even the most recalcitrant waste. Waste can be gasified using pyrolysis or sequestered in glass-like medium through vitrification. Many companies all over the world have started manufacturing plasma assisted waste treatment systems. This chapter discusses the properties of plasma sources relevant to waste treatment and describes many commercialised processes.

18. Greening of the Foundry

Plasma Mediated Metallurgy

Metallurgy is one of the oldest technologies. It also has a very high pollution potential because of the use of complex ores, hydrocarbon heating sources and the resultant emissions. Plasma techniques are invading this field to improve its efficiency, to enable it to use cheaper raw materials and to reduce the environmental impact. This chapter will review major developments in plasma-mediated metallurgy.

19. Wealth from Waste

Plasma Assisted Recycling Processes

Modern concepts in industrial ecology and sustainable manufacturing promote recycling of industrial waste to recover value. Thermal and non-equilibrium plasmas are acquiring an important role as an enabler of this process. This chapter discusses some specific applications where energy and material are recovered from waste using plasma-based processes.

20. A Thousand Suns

Plasma in our Future

The dwindling reserve of fossil fuel is driving the efforts towards developing more sustainable energy sources. Thermonuclear fusion is the ultimate plasma processing where nuclear reaction between light elements releases energy; the process by which stars burn. The fifty year old search for realising fusion has now entered a phase where workable fusion reactors are seen feasible. This chapter discusses the basic concepts of fusion and discusses various approaches to their realisation in the laboratory. Fusion power would be the most precious gift of plasma sciences to humanity.

1. The Age of Perpetual Innovation

Science, Technology and Industrial Revolutions

This chapter reviews the historical role of technology as the tool for the creation of wealth and how industrial revolutions were driven by new technologies. Today's paradigm for knowledge-based manufacturing is based on a number of advanced technologies and incremental advancements. The science of the plasma state of matter has generated enabling technologies, which integrate the unique properties of the plasma state with processes relevant to industrial manufacturing and environmental remediation.

Industrial Revolutions

Technology has now been recognised as the key resource for industrial development and creation of wealth. The history of industrialised nations shows that their development has been based largely on the ability to develop new and appropriate technologies to solve specific problems and to adapt and improve imported technologies to suit local conditions. These countries possess an internal technological dynamism [UNIDO 1993] that assimilated and contributed a steady stream of technical improvements to their methods of industrial production. This flow of technological changes generated a continual increase of the efficiency of industrial development. The increasing opportunities for employment and growth, in turn, created a related improvement in the living standards of their citizens.

Technological changes often come in the form of waves [Schumpeter 1989]. The so-called 'Kondratieve wave' representing wave-like behaviour of economic activity, in this case the whole sale US prices as shown in Fig.1.1. Great Britain in the 1760s to the 1830s witnessed the development of the steam engine, wrought iron, and cotton textiles. These inventions, coupled with a shift to coal as a major energy source and the construction of an inter-linked canal system, fuelled the first long cycle of industrial change. Consequently, power, manufacturing and transportation were highlighted in this phase. The first and second long cycles make up what is commonly referred to as the Industrial Revolution. The second cycle began in Britain about 1825, stimulated by inventions that led to the railroad construction boom of 1838-1843 and the establishment of the telegraphic network. These innovations created a fast, efficient transportation system supported by a new communication network. Together, these systems established an infrastructure, which further expanded the opportunities for economic development. Similar events followed in the United States at a later stage.

Fig. 1.1: The Kondratiev cycle theory holds that capitalist economies grow in a cyclic fashion with an average periodicity of about 53 years.

The third cycle began around 1870. Extractive and heavy industries, power generation, chemicals and infrastructure building were the components of this second industrial revolution. Major technological breakthroughs of this era included the development of steel, widespread application of the internal combustion engine, creation of networks to transmit electricity and the evolution of a manufacturing system based on the principle of mass production and interchangeable parts. Much of the technological innovation in the third cycle was devoted to the development of consumer products and services: trams, telephones, household appliances and so forth.

The fourth long economic cycle had its origins in the Great Depression of the 1930s and its finale in the mid-1970s. The leading economic sectors, which saw some development in this cycle included automobile, electrical, electronics, chemical, and aerospace industries. However, despite the array of technological developments, the only technological innovations of this era were the television, semiconductors, and electronic computers.

The major cycles, and their technological contents, are summarised in Table I. The underlying character of these times was the brutal conquest and plunder of nature. Smokestacks became the symbol of progress. Mass production demanded men to tend machines, and the consequent migration of farm labour to cities brought an unprecedented social transformation. The worker was progressively dehumanised to fit the Ford-Taylor model of work organisation, to enhance productivity. Products were standardised with little choice left to the consumer. This period can be called the machine age, where routine production in large volumes was the norm. But this period is said to have ended with the first oil crisis when the world, for the first time, realised that there were natural limits and constraints to this mode of growth.

The long cycles, which spanned approximately 50 years in length, generally began with a cluster of innovations that occurred during the economic slowdown between cycles. The phases of various levels of exploitation of knowledge, its maturity and deployment between transitions in economic activity is shown in fig. 1.2. While the fifth long cycle is still evolving, it is now widely recognised that the advent of advanced technology was the highlight of the 1980s. The telecommunications and Information Technology sectors have overtaken the auto industry and its ancillaries as the drivers of the world economy. Already, computers and related automation equipment have become the dominant form of capital equipment with software development and maintenance as the major sources of employment.

The New Technological Paradigm

Many social thinkers and writers like Alvin Toeffler [1991], Peter Drucker [2001] and James Brian Quinn [1992] have been heralding the emergence of a new economy based on information and knowledge creation. But the dot.com companies are not the only symbols of this economy, for the nature of manufacturing technologies itself is undergoing a steady change, thanks to the increasingly active and assertive role of knowledge as a production factor. This ‘Sanskritisation of Manufacturing’, has a number of identifying features.

Amalgamation of Research and Production

Flagships of the first industrial revolution, characterised by long-wave economic cycles, with a periodicity of the order of 50 years, known after the Russian economist N. D. Kondratiev and and were Fig. Table 1.2: Technological transition periods between Kondratiev cycles present a favourable window of opportunity for developing countries to enter the new paradigm and to reduce or eliminate their technological gap.

popularised by J. Schumpeter [1989]. Later, perpetual innovation [Morris-Suzuki 1984] and incremental technological advancement replaced these sluggish long cycles. In contrast to government-funded science and technology leading to major breakthroughs and development of new industries, the current technology paradigm is driven primarily by market forces and is focused on continuous improvement and relentless application of technologies to new markets and products. This continual diffusion of technologies has been as radical in its economic and industrial impact as were major breakthrough innovations witnessed earlier (Fig 1.2). Integration of intellectual and manual labour and disappearance of the laboratory-shop floor boundary are intrinsic to this transformation. The knowledge of a worker becomes an explicit factor of production [Nikolajew 1991, Florida 1991] in the new shop floor.

Flexibility

The ability to absorb rapid changes in innovation of raw materials, processes and products characerises the new industrial revolution. Innovator, entrepreneur and consumer form a triad, constantly changing the market and the manufacturing place. Since market demands for products undergo rapid changes, flexibility in tooling and process are imperative. Cluster tooling and software driven flexible process cycles are now integrated into many manufacturing systems. Customised manufacturing even in mass production items like apparels and consumables is now possible.

Convergence

Seamless integration of a mix of technologies is another characteristic of the new economy. For example, the integration of Information Technology and biotechnology has provided the basis for a wide range of new product innovations and business opportunities in many areas. The convergence of advanced manufacturing and agribusiness has led to breakthroughs like robotic combines.

Eco-friendliness

Novel concepts of industrial ecology and green manufacturing have promoted the recycling and the use of waste from one industry as the raw material in another. The most advanced example of this approach is the Danish industrial town of Kalundborg, where a complex industrial symbiosis developed over the last 30 years as firms sought to make economical usage of the waste, partly to minimise the cost of complying with ever-stricter environmental regulations [Grann 1997]. A related development is the emerging concept of dematerialisation and its technological tools, which conserve materials by minimising raw materials and energy requirements. The movement is towards a state of zero emissions, one that closely imitates nature, which as an integrated whole has zero waste. The Zero Emissions Research Initiative [UNU] based at the United Nations University in Tokyo, seeks to improve the profitability of manufacturing while reducing its environmental impact, by finding the missing links among multi-industry clusters of factories.

Humanist Ethics

Ethical concerns of the social impact of science and technology, first expressed coherently at the birth of the atomic age now permeates all areas of research, development and application. The raging debate on genetic engineering is a case in point. The belief that everything that can be invented need not be invented is an expression of this aspect.

Globalisation

The new industrial revolution is also global in its scope, reach and impact. Technologies are sourced internationally and successful innovations are cloned worldwide. Driven by profitability, advanced technologies transcend national boundaries. Manufacturing and services are out-sourced, motivated by concerns of profitability. Ford's assembly line, which is now spread over continents and nations, is a case in point. National boundaries are melting before a new diaspora of knowledge workers. So are markets and raw material sources.

The Knowledge-based Manufacturing

Enabling this transformation from the smokestack to knowledge-based manufacturing is a host of new technologies. While empowerment of manufacturing by knowledge has already taken place, the world today is witnessing the invasion of the factory by the microprocessor and Information Technology.

Microelectronics

The engine driving the new industrial technologies is the microprocessor. Semiconductors, computers and software are the tools of the microelectronics [Luryi 1996] industry. Traditional industries like steel mills, automobile assembly plants and textile mills are increasingly being made intelligent using automation and microelectronic technologies. The versatility of the microelectronics device lies in its amazing ability to shrink in size and cost while increasing its processing power by many folds. Producing a transistor is now cheaper than printing a character in a newspaper. Semiconductor integration technologies combine multiple integrated circuits into efficient modules for performance of complex tasks and are essential for creating economically competitive multi-component systems. Ultra large-scale integrated semiconductor circuits contain structures of sizes of 0.25 μm and less. The next stage of evolution of the microelectronic device technology is the integration of entire systems onto a single chip. The drivers for this are consumer electronics, communications infrastructure, and a host of portable business and personal devices. Together these emerging markets are overshadowing the one-time dominance of the PC industry as a driver for semiconductor technology, and their needs are often quite different from those for personal computer design.

Information technology

The mega change [Naisbitt 1984] from an industrial to information society during which more than half the workers in the developed and many developing countries were engaged in the production and vending of intangible non-good products started in the mid-1950s. The conventional transition of economies from agriculture to manufacturing to services is being replaced by leap-frogging of agricultural economies into the knowledge economy. This is being powered by technologies, which enable the globe to be efficiently and economically linked through the information highways – particularly the Internet.

Information Technology had its origins in the technologies related to the generation, processing, and distribution of information in various forms. It encompasses the collection, storage, processing, dissemination, and use of information. It combines both hardware and software but transcends them by acknowledging the importance of people and the goals they set for this technology, the values employed in making these choices, the assessment criteria used to decide whether one is controlling the technology and is being enriched by it. A subset of it is informatics, which focuses on the impact of information on human life.

Information Technology is a generic term used to cover computers, broadcasting, telecommunications, data networks and the "smart" components becoming increasingly common in cars, TVs and home appliances. Although this infrastructure is technology-based, its most profound effects are on the people and society using it. A networked information infrastructure is well established and expanding rapidly as demand for services is rising. The networked iformation infrastructure includes the telephone system, the Internet, fax machines, and computer networks.

Internet, the evolving international information network is a most remarkable development. First designed in 1969 as a part of a US Defence Department project [Connected], the Internet community now comprises more than 20 million users in 180 countries. This development may prove as significant as the invention of the microprocessor or the IBM PC introduced in 1981 [Gates 1995]. The Internet is expected to continue its expansion and diversification over the next five years, especially in the area of electronic commerce through both business-to-business use and in on-line home shopping. Goods sold electronically can be 40% to 50% cheaper than those sold by conventional means, mainly because of the huge size of the market.

Biotechnology

The broad and heterogeneous field of applied biological sciences [Robbins-Roth 2001, Rudolph 1996], deals with the genetic engineering of bacteria and yeast, culture of hybridoma to produce monoclonal antibodies, fermentation processes and synthesis of organic chemicals through biological routes. It has already made significant impact on chemical, pharmaceutical, agriculture and food industry. About 60% of enzymes are the product of modern biotechnology even as new uses are being developed for environmental, food, agricultural and textile industry. Environmental biotechnology or bioremediation focuses on the development of products and techniques for cleaning up pollution caused by agriculture, industry and urbanisation.

Micro-organisms produce many industrial biotechnology products, such as beer, antibiotics or enzymes. Cells from organisms, plants or animals grown artificially are used to produce large amounts of valuable products. A valuable purple dye called shikonin, once produced in Japan from a plant that is almost extinct is now harvested from cells in culture within just 20 days [Curtin 1983].

Bio-catalytic enzymes speed up and direct chemical reactions. While some biotechnological processes use whole organisms (e.g. yeast to make wine), others use enzymes that have been purified from the organism that manufactures them (e.g. enzymes in detergents to dissolve grease and protein). Besides these, speciality enzymes are finding increasing uses in the development of new drugs and antibiotics, as well as medical diagnostics and analytical uses. Enzymes often work at lower temperatures and pressures, and therefore save energy. In fact, many enzymes are more efficient than their chemical counterparts. Moreover, doing away with toxic chemical solvents reduces waste and pollution. Many enzymes are specific, producing more of the desired product, and fewer toxic by-products. Enzymes can carry out reactions for which there are no known chemical catalysts; these are finding uses for making speciality chemicals and new drugs.

Advanced Manufacturing Technologies

A number of advanced manufacturing technologies have already invaded production systems. Net shape processing creates an object in near-finished form, thus dispensing with the need for labour intensive finish machining and leads to quicker production, fitting well with the lean production paradigm. Rapid solidification processes allow the creation of new alloys and compositions by adding molten metals in controlled amounts directly into the solid phase. These have unusual physical properties including high strength. Moreover, surface engineering techniques offer a way to tailor the surface properties of a material without changing the bulk properties. This allows very hard cutting tools to have great strength and toughness, for example, or allowing materials to survive very corrosive conditions. Surface treatments provide better finishes and higher quality materials for several industries and applications.

Ultrapure Materials

Ultrapure materials [NAP 1989] play an important role in a number of commercial applications. Development of extremely pure semiconductor crystals is essential for integrated circuits, optoelectronics and photonics. Chemical vapour deposition techniques have been used to create a pure silicon layer used to build the actual devices on top of a wafer. Consequently, increasing the purity of the underlying ingot has become relatively less important to microelectronics. Some processes, such as silicon-on-insulator, even obviate the need for very pure ingots.

Ultrapure materials are also important for structural applications, since microscopic impurities can cause cracks in ceramics and ceramics-based composites. In general, ultrapure refining methods include micro-gravity and high- pressure fabrication methods, which suppress convection currents in the material and allow even distribution of impurities or their elimination. The ability to create ever-larger ingots of pure silicon remains important to advanced microelectronics.

Predictive process control, which integrates sensors, data communications and processing, and modelling is critical to these manufacturing technologies. Improved interfaces with operators, usually via graphic displays, will also provide improved control over system performance. The most important class of sensors for this sub-area is non-imaging sensors, which can be used to measure a vast range of parameters such as temperature, pressure, humidity, radiation, voltage, current, or presence of a particular chemical or biological material. In addition to passive sensors, there are active sensors usually based on laser technology. Specialised microsensors, on the other hand, are used to detect particular chemical or biological agents. The information generated by the sensors must be combined and processed using data processing and models specific to the process being monitored.

Artificial Structuring Technologies

Artificial structuring of materials refers to the ability to combine materials on a microscopic level. This small scale ordering using thin film deposition technologies makes it possible to generate novel properties that are non-obvious and unpredictable on the basis of the properties of the precursor materials. They, however, provide the ability to generate new materials and dimensional scales. The current manufacturing efforts such as sputter deposition and spin-on coating technologies are being slowly replaced by more advanced techniques such as chemical vapour deposition and molecular beam epitaxy.

Artificial structuring methods drive the growth in defence, Information Technology, manufacturing, energy, and transportation systems. From a commercial perspective, these techniques have produced tremendous growth in microelectronics, high-density data storage, and photonics. The dependence of information and communication technologies on such products highlights the importance of their underlying manufacturing capabilities. Future development of microelectromechanical systems also depends on the precise control of the properties of thin films. The evolution of more sophisticated manufacturing techniques is critical to the realisation of advanced coatings with enhanced hardness, corrosion- resistance, thermal, and wear characteristics. Large-scale production of high-quality diamond thin films with high hardness, wear-resistance, and very good thermal conductivity at extremely low temperatures is an example.

Emergent Technologies

The manufacturing process is likely to undergo a radical transformation in the future if the new approaches, at present still in the laboratory stage, invade the manufacturing space. These technologies symbolise the evolution of manufacturing towards a state of zero emission, high value addition and use of dispersed methods. Early twenty-first century will be the time when these radically new technologies enter the industrial arena.

Nanotechnology

Nanotechnology [Dressler 1986] exploits the possibility of atomic-scale assembly to form precise mechanical structures of molecular dimensions. Nano-clusters, layers, tubes, and two- and three-dimensional structures constitute the family of nanoentities. These constitute the precursors for building up functional assemblies. The present level of development of nanotechnology is comparable to that of computer and Information Technology in the 1950s. New techniques and the discovery of novel phenomena and processes have opened revolutionary vistas for developments in nanostructured materials, and nanodevices.

Engineered nanostructures include nanostructured materials such as ceramics, optical materials, polymers, and metals; nanocomponents such as coatings and connectors; and nanodevices such as sensors, switches, and reactors. Applications will permeate into pharmaceutical and chemical industries, electronics, space exploration, metallurgy, biotechnology, cosmetics, the food industry, optics, medicine and metrology.

Material engineering at the nanoscale should be able to produce uniform voids with atomic dimensions, thereby cutting the mass, cost, energy, and time needed for production. For objects with structural loads in pure compression or mixed compression and tension, the void fraction could be as high as 99% leading to immense material saving. Incorporating voids, combined with scavenging heavy pre-nanotechnology parts, will allow us to recycle old systems into multiple new ones without additional material resources, reducing the need for mining and refining. Manufacturing techniques based on nanotechnology should yield great increases in productivity and wealth. The requirement for low cost drives the demand for self-replicating manufacturing systems, the so-called Von Neumann machines [Neumann 1966].

Microelectromechanical Systems

The technological and cost advantages realised in miniaturisation of electronics devices are driving similar concepts in mechanical systems. Three dimensional structures and devices with dimensions of the order of micrometers, which will merge sensing, computing and actuating will revolutionise the link between the electronic intelligence and the tactile world. Integration of all these functions into a single device will bring enhanced levels of perception, control, and performance – these devices will be able to sense and control motion, light, sound and heat in the world of the future. The two enabling technologies of microengineering [Trimmer 1990] are microelectronics and micromachining. Microelectronics, producing electronic circuitry on silicon chips, is already very well developed. Micromachining, on the other hand, is the technique used to produce the structures and moving parts of microengineered devices.

Microdevice manufacturing technologies have the potential to change and influence areas as wide ranging as automobiles to satellites. Many machine tools can be significantly improved with better sensors and finer control. Microdevice manufacturing technologies may make possible new classes of much lighter satellites. Many microsensors, including biosensors and chemical sensors, have the potential for mass production once the individual steps are created. Thus, microfabrication techniques have become very important to sensor technology as miniaturised, integrated systems have become possible. In the longer term, there is a possibility of creating integrated computers and small machines for a variety of applications.

One of the main goals of microengineering is the integration of microelectronic circuitry into micromachined structures to produce completely integrated systems called microelectromechanical systems (MEMS). Such systems could have the same advantages of low cost, reliability and small size as silicon chips produced in the microelectronics industry. Experts claim that in the next 50 years the structural engineering of micro-silicon devices may have as profound an impact on society as the miniaturisation of electronics did.

Self-Assembling Materials

Living organisms grow and multiply by a process of self-assembly following a code of construction in-built in the components of its assembly such as cells. This is called coded self-assembly. Raindrops take on spherical shape to minimise the surface energy. Water drops on the surface of leaves assume spheroidal shapes. These are examples of thermodynamic self-assembly. This magic of nature is mimicked in the science and technology self assembled materials or SAMs, where materials are prepared with a set of built in instructions for assembly. A self-assembling process [Whitesides 1995] is one in which atoms, molecules and aggregates of molecules arrange themselves into ordered functioning entities without human intervention. Crude forms of self-assembly are already in industrial practice, for example float glass manufacturing uses the property of low melting point dense metals like Indium to support molten glass and produce smooth regular surface. Crystal growth is another example where complex crystals grow without human intervention. Self-assembly also produces carbon nanotubes, which consist of several nested concentric cylinders of carbon.

Concepts of deliberate design and manufacturing of materials and assemblies using the principles of coded and thermodynamic self-assembly are beginning to be implemented in the laboratory. Cross-disciplinary inputs such as concepts of positional assembly and self-replication in nanotechnology will accelerate the growth of this technology. The advantages are immense: manufacturing will move completely away from the wasteful practices of second wave culture – in short, the factory of the future will become a womb reflecting the process of life itself.

Smart Materials

The basic principle behind traditional design and manufacturing is the anticipation of failures and the worst-case scenario of failure. Here the recipe is usually substantial overdesign and use of excess materials. Designs usually contain large margins of safety in terms of reinforcements, redundancy, backup subsystems and added mass.

Smart materials [Worden 2003] will have the in-built ability to modify their behaviour in response to external conditions. Materials that allow structures to adapt to their environment are known as actuators in that, they can change shape, stiffness, position, natural frequency and other mechanical characteristics in response to external stimuli. The four common actuator materials are shape memory alloys, piezoelectric ceramics, magnetoresistive materials and electro and magnetorheological fluids. Piezoelectric materials elongate and contract in response to an applied voltage and are useful for precise, high-speed actuation. Magnetostrictive materials are the magnetic equivalent of piezoelectric materials. Rheological fluids contain micron-sized particles that form chains when placed in electric and magnetic fields resulting in increase of viscosity by orders of magnitude. Nitinol, a nickel titanium alloy developed at the Naval Ordinance laboratory in US has the ability to revert back to its original shape even after being elongated upto 8 percent of its original length. Nitinol is being used as micromanipulators and robotic actuators to mimic human muscles.

Plasma Enabled Processing

The tools of transformation to the post-industrial manufacturing are all characterised by one common feature; they are all minimalist in concept, utilisation of materials and execution. Synthesis is almost on atomic scale and functional to the core. The tools that will make these machines are equally exotic and one such tool is plasma enabled processing.

Plasmas are ionised gases with free electrons, ions and excited neutrals. While the charged particles can respond to external electromagnetic energy fields and transport energy, the fluid properties are enhanced by the particles setting up internal self-consistent electric and magnetic fields, resulting in collective effects like flows, waves, in-stabilities and self-organisation. Each specie may have independent energy distribution, not necessarily in equilibrium with other species. The internal energy is composed of thermal, electric, magnetic and radiation fields, whose relative magnitudes allow the plasma state to exist in an extended, multi-dimensional parameter space. The parameter space of naturally occurring and man-made plasmas is shown in Fig. 1.3.

Plasma-enabled processing (PEP) exploits plasma as an industrial tool. As an example of knowledge based post-industrial technology, it is environmentally benign, clean, energy efficient with Fig. 1.3: Plasmas exist in a wide parameter range. They can be naturally occurring or man-made.

very little effluents and emissions. Its ability to integrate multiple process steps leads to high throughput and increased efficiency. Multitasking in a single reactor leads to fast response to changing market demands and lower capital cost. Control is fast and precise and amenable with computers improving its reliability

When materials are exposed to plasmas, a variety of physical, chemical and metallurgical transformation of the material takes place. PEP integrates the plasma-material interaction phenomena with the manufacturing process. PEP technology adds value to conventional materials and makes new types of materials and material processing techniques possible. Experts claim that PEP will have a direct impact on the world economy in virtually every aspect of industry, both traditional as well as high tech. It has an astonishingly wide range of applicability with beneficiaries ranging from astronauts to art connoisseurs.

The economic impact of plasma enabled processing can be measured with the help of a number of indices. A trivial measure is the market for plasma processing equipments and products, which by conservative estimates, runs into hundreds of billions of dollars. Lifecycle enhancement of products such as engineering tools and components through plasma assisted modification of surface and near surface properties is an important index of the economic impact. Dematerialisation, which is the minimisation of materials, energy and process in manufacturing, is another index, dramatically illustrated in the plasma processing of integrated electronic components. The improvement of environmental quality by treatment of industrial emissions by nonequilibrium plasma chemistry, of which decarbonisation, which reduces the negative economic impact of carbon pollution by treatment at the source is a subset, is yet another measure. Finally the economic significance of the contribution of plasma processing to consumer products ranging from anti-reflection ophthalmic coating to giant plasma display panels for high definition television cannot be forgotten.

A recent US National Research Council report [NRC 1991], indicates a number of important uses of plasmas including hardening of tools, pasteurisation of foods, decorative laminations, sterilisation of medical products, environmental cleanup, gas discharges for lighting and lasers, high definition television, isotope separation, electrical power switching, cutting and welding technology, and plasma-based space propulsion systems.

The pervasive influence of plasma technology is seen all around us. High efficiency lighting is perhaps the best example. There are primarily two types of plasma-based light sources, fluorescent lamps and high-intensity arc lamps. Fluorescent lamps find widespread use in homes, industry and commercial settings. Inside every fluorescent lamp it is the plasma that converts electrical power to ultraviolet light that causes the lamp's phosphor coating to produce the light we see. High-intensity sources are widely used in industrial and commercial settings as well as for outdoors and security lighting near homes and public areas.

A striking example of a plasma product is the Pentium chip where 500 million micron sized transistors, capacitors, resistors and diodes are formed on a silicon substrate and wired together to form circuits in approximately one square cm. area. These devices power home computers, TVs and electronics. Plasma display panels are slowly replacing the bulky cathode ray tube displays in the television. They consist of millions of pixels made from tiny gas discharge plasma sources. The construction has two glass plates, each containing parallel electrodes, sealed to form an envelope filled with a neon and xenon gas mixture. A gas discharge plasma is created by applying an electric field between the electrodes. Each pixel consists of three sub-pixels, one each of red, green and blue. By combining these primary colours at varying intensities, all colours can be formed.

Plasma systems make possible new methods for surface cleaning and sterilisation for food, medical, and other applications. In contrast to heat sterilisation, which is slow, and irradiation damaging to materials, this new plasma technology has been shown to kill bacteria on various surfaces within seconds. In addition to destroying bacteria, such plasma systems also destroy viruses, fungi and spores. These systems also provide an environmentally benign method for pre-treating surfaces.

Plasmas can mediate in producing wear and corrosion resistant hard coatings on engineering tools, increasing tool life and enhancing productivity. Small plasma reactors are placed in the exhaust of automobiles for the removal of the noxious nitrogen oxides emitted by petrol burning engines. Scaled up versions will clean emissions from coal burning power stations.

As such, the combined world market for plasma-enabled technologies is estimated at 200 billion US dollars per annum [NRC 1986]. These include markets for coating of materials ($50B); waste processing ($50B); plasma electronics including flat panel displays and high power switches ($40B); high performance semiconductors and integrated circuits ($30B); high performance ceramics and other applications ($20B).

Plasma Sciences

Plasma, the fourth state of matter, has been traditionally studied in the context of astrophysics, magnetohydrodynamic power generation and thermonuclear fusion research [NRC 1986]. The major impetus for the growth of plasma sciences came from the search for conditions in which fusion of deuterium and tritium nuclei to form helium would yield nuclear energy [Fig. 1.4]. Similar nuclear reactions make the stars burn and give hydrogen bomb its awesome destructive power. To release this energy in a controlled manner on the earth requires many conditions to be simultaneously fulfilled. The plasma must have a temperature of 100 million degrees so that the natural tendency of the nuclei to repel each other can be overcome and they can come close enough for nuclear forces to take over and fuse them. It must be confined long enough for fusion reactions to release more energy than was expended to heat it. The product of density and confinement time must exceed 10^{14} seconds per cubic centimetre; this is the so-called ‘Lawson Criterion’. The plasma should also be insulated from the surroundings so that they would not lose heat or get contaminated by other material, which can affect the fusion yield.

Fig. 1.4: The "D-T" reaction has the highest reaction rate at the plasma temperatures, which are currently achievable, which makes it the easiest reaction to use in a man-made fusion reactor.

Major efforts in fusion research started in the 1950s. The approaches to achieving fusion conditions have taken two directions. In one, called inertial fusion, intense pulses of laser and particle beam energy irradiate minute solid pellets of fuel. The outermost layer absorbs the laser energy and ablates outwards. The resulting inward reaction on the rest of the pellet produces compression and heating. The compression of the pellet and the fusion burn would take place for less than a microsecond. For example, the National Ignition Facility being built in the United States will use 192 laser beams applying 1.8 Megajoules of energy to prove this concept.

The other approach is to confine low-density plasmas in magnetic traps and heat them using a variety of energy sources like large currents, intense radio frequency fields or energetic neutral beams. The most successful of such traps is the tokamak, invented by Russian scientists, Igor Tamm and Andrei Sakharov. Tokamak has a tyre shaped vacuum vessel, which is filled with low-pressure mixture of deuterium and tritium. A magnetic coil wound around the chamber produces a toroidal magnetic field. The current flowing in the toroidal plasma heats the plasma by ohmic dissipation. This current also produces a poloidal magnetic field, which, in conjunction with the external toroidal magnetic field produces confining magnetic surfaces to which the plasma particles stick.

The early phase of fusion research had a brute force approach, pumping in more and more electrical power into the ionised gas with the objective of heating the plasma. Internal thermal energy was lost through mysterious channels. Realisation slowly dawned that we were dealing with a new state of matter whose properties were not known very well. To overcome this impasse and to make further progress in fusion, the entire field of plasma physics had to be invented.

Harnessing fusion energy still has a long way to go. Part of the problem lies in the mastery of a number of very difficult technologies. To get economically viable fusion yield, the fusile matter has to be heated to at least a hundred million degrees, where it exists in the fully ionised state. The hot plasma can be confined only by magnetic fields of specific and very often, complex topologies. The heat insulation of the magnetically confined plasma is imperfect and even now incompletely understood. To heat the plasmas, currents of the order of millions of Amperes have to be induced inside the plasma, and further irradiated by intense electromagnetic fields and particle beams with power density in the range of megawatts/sq. meter. The hot, magnetised, current carrying plasma exists in a delicate equilibrium and develops instabilities at the slightest provocation, dumping mega Joules of energy in milliseconds into the walls and magnetic field coils. The helium ash as well as impurities generated by the interaction of the plasma with the confining walls will have to be exhausted before they poison the plasma and cool it by radiation. The fusion core has to be coupled with neutronics to tap the neutron energy through conventional thermal cycle. These formidable problems, as well as issues like the grid impact of large fusion systems, radioactivity in the first generation DT fusion reactors, reliability of technology and the economic viability have generated as many detractors of fusion as there have been champions.

Today the promise of fusion is on the verge of fulfilment, as laboratory devices have shown that fusion was indeed feasible in the laboratory. Experiments such as the Joint European Torus at Culham, UK and the Tokamak Fusion Test Reactor at Princeton, USA have demonstrated the scientific feasibility of fusion through experiments in which fusile Deuterium-Tritium plasmas were burned to produce thermonuclear neutrons, albeit, at low power levels of the order of a few megawatts.

The next step towards the goal of power producing reactors is the International Experimental Tokamak Reactor (ITER). Mikhail Gorbachev first proposed building such a reactor as a multinational endeavour in 1985 and a group of scientists from various countries have been working on the design of such a device ever since. European Union, Japan and Russia have been enthusiastic supporters of ITER. Recently US have rejoined the project and China and South Korea also have become members. ITER project, hitherto under the auspices of the International Atomic Energy Agency, is in the transitional phase before becoming an autonomous multinational project. Another issue yet to be addressed is the location of the ITER. When finalised, the host country would enjoy significant benefits and would be expected to make a greater financial contribution as a result. From this reactor to commercialisation is yet another step, at present too far into the future to make any realistic guess as to when fusion would yield commercial power.

Astrophysical and Space Plasmas

Man’s yearning to understand the universe provided another driving force for the growth of plasma sciences. The plasma environment affects many of the phenomena in space. Close to earth there is a layer of plasma called ionosphere produced by the photo-ionisation of the air by the ultra-violet light from sun. Radio communication between distant regions on the earth is possible because this layer reflects radio waves. Beyond this the magnetosphere shields the earth from the high velocity solar wind. Besides, the violent upheavals on the sun called solar flares are plasma phenomena. The solar plasma interaction with magnetosphere and ionosphere and the resultant electromagnetic perturbations, which affect communications, has spawned the field of ‘space weather’. While forecast of space weather is important for global communications, the properties of space plasmas are important in determining the capabilities and longevity of spacecrafts.

The dusty plasma surrounding comets and planetary rings is another recent entrant to the growing spectrum of space plasma phenomena. Plasma physics is also relevant to many areas of astrophysics ranging from stellar and interstellar plasmas to star clusters and galaxies. Examples where plasma physics already has made significant impacts include models of magnetised accretion disks and associated jets and winds. Mechanisms of particle acceleration in plasma shock waves are central to understanding cosmic ray acceleration. Although in-situ observations using satellites and exploratory space probes are essential to understand these phenomena, they are expensive and time consuming. To understand these phenomena better, one must integrate our knowledge of plasma physics with space sciences.

Birth of Plasma-Enabled Processing

The search for the star fire in the laboratory has been a highly visible and quite often controversial application of plasma sciences. Excessive public attention to this has often relegated the other practical applications of plasmas to the background. While the potential benefit to society through the fusion route to energy production is enormous, practical power-producing fusion reactors are many decades into the future.

Plasma processing has always been inventor-driven. Science has generally followed applications. Arc technology was applied to metallurgical processes in 1890. Plasma techniques were applied to industrial applications as early as 1905 in Norway. Some major milestones in the application of plasma processes in industries are given in Table 2

Fusion research, however, was the prime driver for the development of a host of technologies for producing and manipulating plasmas of an extended parameter space and understanding their interaction with matter and electromagnetic fields. This has led to the large-scale nucleation and growth of the industrial applications of plasma enabled processing. The early phase of applications exploiting the thermal energy of plasmas gave way to utilisation of the physico-chemical properties of plasmas. Rapid growth of this field started in the seventies when it became an enabling technology for semiconductor device fabrication. Parallel developments in applications also took place in modification and engineering of surfaces with plasmas, synthesis of advanced materials in thermal plasmas, development of advanced coatings and films etc.

The growing perception of the strategic importance of plasma enabled processing is reflected in intensification of efforts in structuring research linkages with industries. Many countries have now adopted the so-called 'plasma initiative'. The declining fortunes of fusion research also helped this indirectly as a large number of plasma scientists began to look for new research opportunities in different areas of application.

Recommendations by the National Materials Advisory Board, USA led to the establishment of the Engineering Research Centre Program designed to link academic engineering research and education to engineering practice. The Plasma Aided Manufacturing Engineering Research Centres at the Universities of Wisconsin, Minnesota and the Drexel were set up under this programme. Their specific mission was to adopt the substantial body of knowledge already existing in various engineering and scientific disciplines to plasma aided manufacturing, to achieve long and short-term usefulness in industry. The goals of the Engineering Research Centres are:

To develop new processes to ensure that plasma aided manufacturing will satisfy the present and future requirements of the industry.

To develop new diagnostics, sensors, modelling, statistical and control strategies for plasma aided manufacturing.

To conduct the necessary engineering support studies needed to fulfil these missions.

To provide a unified, cross-disciplinary experience for the large number of students interested in entering this exciting and demanding field of high technology and to expose a large segment of the graduating engineers to new concepts of design and system integration in this area

To foster and maintain strong relationships between universities, industry and government for information exchange and technology transfer.

The major US fusion research laboratories are also linked to the industry through various technology spin-off programmes. In Small Business Innovative Programme (SBIR), small business is funded to meet federal research objectives through selected technology development, which are then commercialised by the company. Other modes of technology transfer include Small Business Technology Transfer (SBTT) programme and Co-operative Research And Development Agreement (CRADA). The Pulsed Electric Field sterilization of food products is a typical product developed under this programme. Princeton Plasma Physics Laboratory is collaborating with Dupont, BASF and Wellman through the Princeton textile Research Institute for the development of diagnostics to monitor textile processing. Lawrence Livermore National Laboratory, along with other Department of Energy (DoE) laboratories such as Sandia National laboratory and Lawrence Berkeley Laboratory is teaming up with major semiconductor manufacturers like Intel, Motorola and Advanced Micro to develop extreme ultraviolet lithography technology. MIT's fusion laboratory has spun off Plasma Enhanced Melter for waste treatment with thermal plasmas.

The European Fusion programme performed under the overall umbrella of European Fusion Development Agreement (EFDA), has an active programme to spin off fusion related technologies for commercial exploitation. UKAEA's fusion activities have initiated unique outreach activities by setting up the Culham Innovation centre.

Plasma science is a well-established research topic in British universities. While the origins of this strength lie in past funding of the fusion and space programmes, many plasma groups have developed much wider interests and expertise with many techniques ranging from laser diagnostics to advanced computational modelling. A substantial body of expertise exists which could be tapped in the context of technological and industrial plasma applications. A recent study for SERC (now EPSRC) identified 27 well-established academic groups working in plasma physics and chemistry of which 12 already had interests in technological applications

The Center for Exploitation of Science and Technology (CEST), an industry-sponsored think tank, launched its Plasma Initiative in 1991 to review the current exploitation status of plasmas and to explore ways in which the evident discontinuity existing between industrial needs and supply of expertise could be effectively bridged. The report 'Industrial Plasmas - Focusing UK Skills on Global Opportunities' [CEST 1992] recommends an integrated exploitation approach by improving the science-base and potential industrial users. They helped set up the UK group on Plasma and Ion Beam Surface Engineering (PISE UK) and recommended to the Science and Engineering Research Council (SERC) to develop an integrated management approach to research support across the Physics and Engineering boards and the Material Commission. Another recommendation is towards creating an umbrella organisation on plasmas by integrating the PISE UK with the British National Committee on Electroheat. A UK Plasma Engineering Center to engage researchers more closely and in greater numbers to industrially relevant, end-user focused projects has been established at the University of Hull.

Major German manufacturing concerns have recognised the vital role of surface engineering in their business and treat it as the next big step forward in manufacturing technology. German federal and state governments match the corporate commitment. In 1983, the German Joint Committee on Plasma Surface Engineering was formed and in the period from 1988 to 1996, the Federal Ministry of Education and Research (BMBF) support was focussed on thin film and surface coating technologies [BMBF 2001]. Since 1993, the BMBF support covers a wide area of plasma technology. The state governments are also stimulating individual initiatives between local industry and universities. More than 2400 companies use some variety of plasma surface engineering. The annual growth in applications distributed among PVD, CVD, ion beam and other plasma treatments is estimated at over 20 %.

Parallel to what happened in fusion research, there is a growing realisation that strengthening the science base was important to break the technology limits. Powerful experimental, diagnostic and computational tools originally developed for fusion became increasingly adapted to research in plasma assisted material processing.

I would like to conclude this chapter by mentioning an initiative by the Institute for Plasma Research (IPR) in India in building an institute-industry bridge for addressing the problems of commercialisation of plasma assisted material processing technologies by setting up the Facilitation Centre for Industrial Plasma Technologies (FCIPT) in 1997 [John 2002]. The centre consolidates all activities related to technology development, demonstration, incubation and commercialisation and links IPR with the Indian industry [Fig. 1.5]. FCIPT has established a multi-disciplinary group of physicists, material scientists, chemists and engineers and infrastructure for process and instrumentation development for plasma technologies. The centre has prototypes and pilot plants for industrial scale job working to generate the database on instrument performance, process reliability and economics. Industry, research establishments and universities extensively use an advanced material characterisation facility. Facility to manufacture complete reactors and supply them to industries and research institutions is an integral part of the technology transfer activity.

Fig. 1.5. Photograph of the Facilitation Centre for Industrial Plasma Technologies established for the commercialisation of plasma technologies developed at the Institute for Plasma Research, Gandhinagar, India

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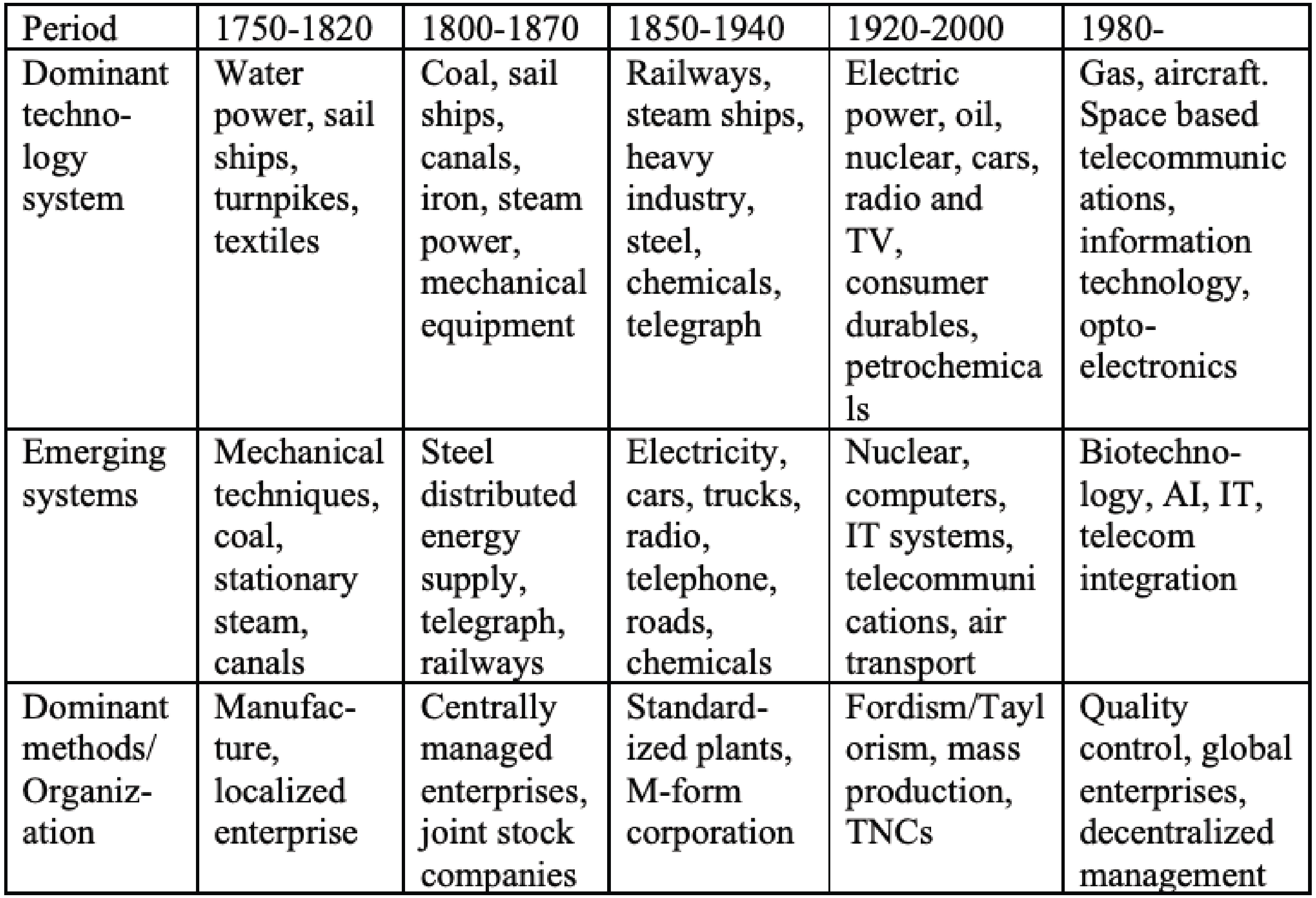
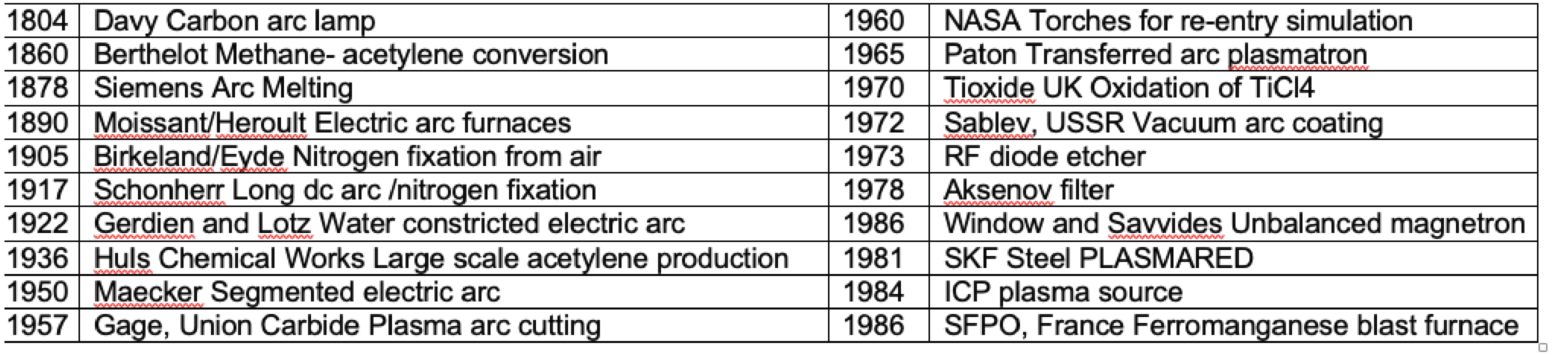


Period	1750-1820	1800-1870	1850-1940	1920-2000	1980-
Dominant techno-logy system	Water power, sail ships, turnpikes, textiles	Coal, sail ships, canals, iron, steam power, mechanical equipment	Railways, steam ships, heavy industry, steel, chemicals, telegraph	Electric power, oil, nuclear, cars, radio and TV, consumer durables, petrochemicals	Gas, aircraft. Space based telecommunications, information technology, opto-electronics
Emerging systems	Mechanical techniques, coal, stationary steam, canals	Steel distributed energy supply, telegraph, railways	Electricity, cars, trucks, radio, telephone, roads, chemicals	Nuclear, computers, IT systems, telecommunications, air transport	Biotechno-logy, AI, IT, telecom integration
Dominant methods/ Organiz-ation	Manufac-ture, localized enterprise	Centrally managed enterprises, joint stock companies	Standard-ized plants, M-form corporation	Fordism/Taylorism, mass production, TNCs	Quality control, global enterprises, decentralized management

Table 1: Clusters of pervasive technologies: systems and organization



1804	Davy Carbon arc lamp	1960	NASA Torches for re-entry simulation
1860	Berthelot Methane- acetylene conversion	1965	Paton Transferred arc plasmatron
1878	Siemens Arc Melting	1970	Tioxide UK Oxidation of TiCl4
1890	Moissant/Heroult Electric arc furnaces	1972	Sablev, USSR Vacuum arc coating
1905	Birkeland/Eyde Nitrogen fixation from air	1973	RF diode etcher
1917	Schonherr Long dc arc /nitrogen fixation	1978	Aksenov filter
1922	Gerdien and Lotz Water constricted electric arc	1986	Window and Savvides Unbalanced magnetron
1936	Huls Chemical Works Large scale acetylene production	1981	SKF Steel PLASMARED
1950	Maecker Segmented electric arc	1984	ICP plasma source
1957	Gage, Union Carbide Plasma arc cutting	1986	SFPO, France Ferromanganese blast furnace

Table 2: Some Milestones in Plasma Technology Development

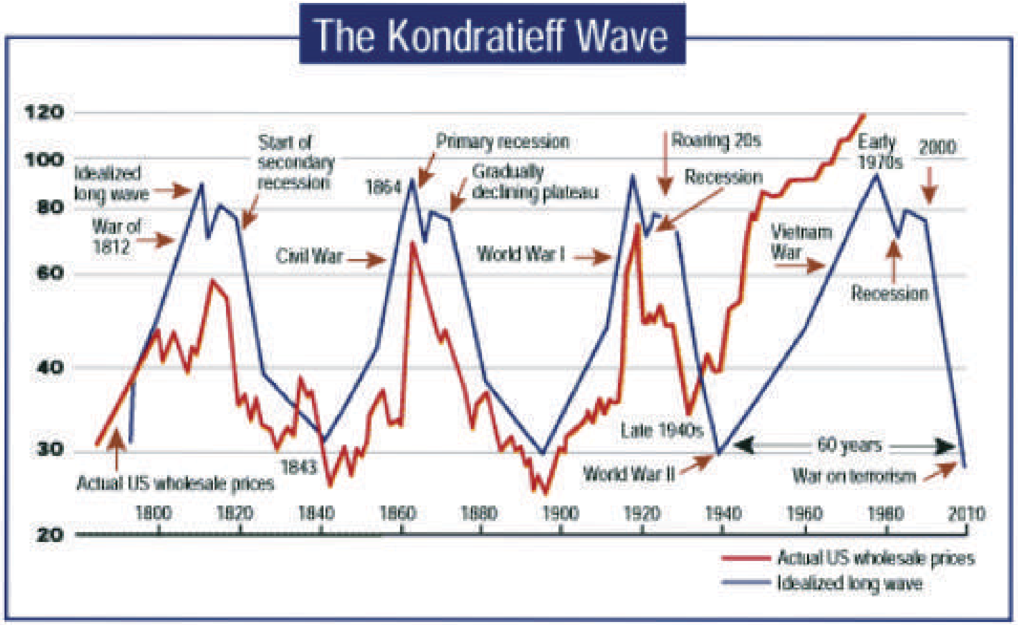
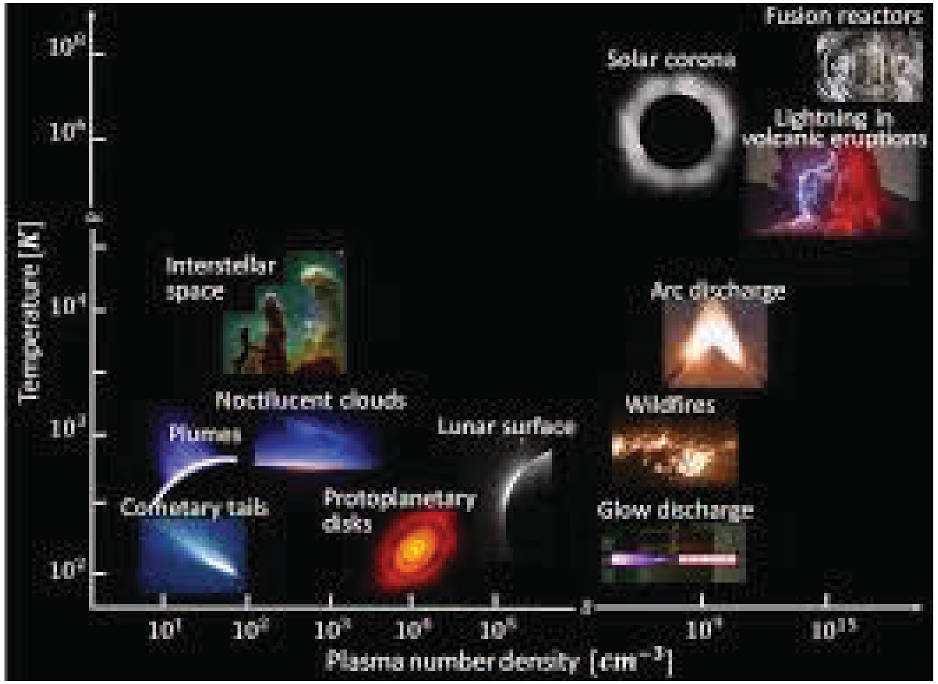


Fig. 1.1: The Kondratiev cycle theory holds that capitalist economies grow in a cyclic fashion with an average periodicity of about 53 years.



1.3: Plasmas exist in a wide parameter range. They can be naturally occurring or man-made.

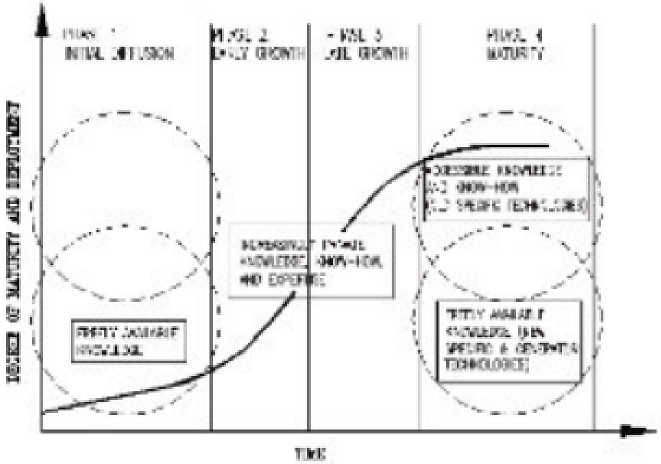


Table 1.2: Technological transition periods between Kondratiev cycles present a favourable window of opportunity for developing countries to enter the new paradigm and to reduce or eliminate their technological gap.

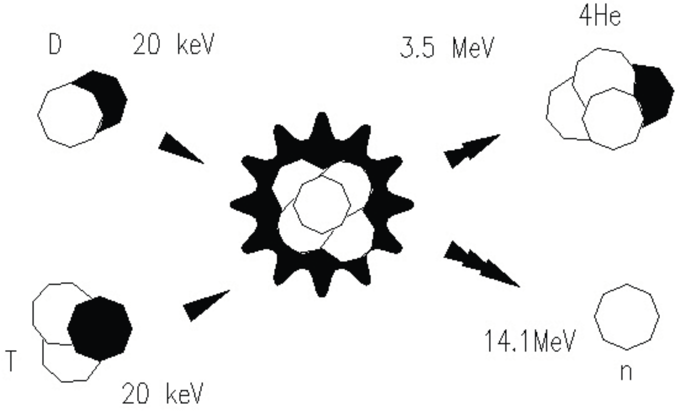


Fig. 1.4: The "D-T" reaction has the highest reaction rate at the plasma temperatures, which are currently achievable, which makes it the easiest reaction to use in a man-made fusion reactor.

Fig. 1.5. Photograph of the Facilitation Centre for Industrial Plasma Technologies established for the commercialisation of plasma technologies developed at the Institute for Plasma Research, Gandhinagar, India

2. The Fourth State

The Physics and Chemistry of the Plasma State

Solid, liquid and gas are familiar states of matter. The constituents of these states are atoms and molecules. The transformation of one state to another is achieved by heating. Transformation to a fourth state of matter takes place, when the gas is heated to very high temperatures, or when subjected to energetic radiation (fig.2.1). The atoms are further broken down into electrons and ions and the neutral atoms are chemically transformed. This fluid consisting of charged particles and neutral atoms and molecules is called the plasma. Though less familiar to us, plasma is the most abundant form of matter in the universe. Sun, other stars and the interstellar matter exist in the plasma state.

We can identify several basic species in a plasma:

Free electrons with energy depending on their translational speed or equivalent temperature designated in electron volts. One electron volt is equivalent to 11,600 degrees.

Ions are molecules or atoms, which have lost one or more electrons. There can also be negative ions, formed by electrons attaching themselves to the atoms of electronegative gases like oxygen.

Atoms and molecules, which consist of nuclei with positive charge, surrounded by bound electrons rotating around the nuclei. These can be in their ground state or excited states.

Photons created within the plasma by interactions between the plasma species.

Ionisation Processes

Ionisation is the process of separating electrons from the nuclei to which they are bound (fig.2.2). Many types of ionisation processes are possible:

Heating a gas to a high temperature can lead to thermal ionisation. The temperature and the degree of ionisation are related to each other by the Saha equation. Since temperatures of the order of few thousands degrees Kelvin are required, plasma production on a continuous basis by thermal ionisation is not convenient. Transient heating by gas dynamic shocks and chemical means can result in thermal ionisation.

Chemi-ionisation: In certain chemical reactions the energy released in the formation of chemical bonds is sufficient to ionise the products of the reaction. Ions are produced in a flame by chemi-ionisation, in *e.g.*, $CH + C_2H_2 \rightarrow C_3H_3^+ + e^-$. The chemi-ionisation rates are quite low.

Irradiation of a gas by ultraviolet or soft X-ray photons can result in ionisation. This is how ionosphere, the plasma mantle of the earth's atmosphere, is formed. However photo ionisation cross-section being of the order of 10^{-18} cm^2, extremely intense ultraviolet and vacuum ultraviolet photon sources are needed to make this process work on a practical basis.

When atoms impinge on a metal surface and evaporate, it can lose an electron and become an ion under certain conditions. The primary conditions are that the ionisation potential of the atoms should be less than the work function and that the surface should be hot enough for the atom not to be adsorbed on condense on the surface. This process is called surface or contact ionisation.

Irradiation of a gas by pre-accelerated electron or ion beams can result in ionisation and plasma production.

The electron impact ionisation for most atoms has a cross-section of 10^{-16} cm^2 when the ionising electron has energy of about 100 electron volts. This energy can be given to electrons in an electric field (fig.2.3). Hence the most popular and convenient means of plasma generation is through electrical discharges where electrons are energised in an ambient electric field and made to collide with atoms producing ionised species.

Lightning is an example of plasma formed in nature by electrical discharge in the atmosphere. Tiny ice crystals moving in updrafts get charged by collisions with clumps of hail and transfer the charge to the cloud. The negative voltage at the base of the clouds produces an electrical discharge to the ground. The spectacular show of light and sound is a consequence of the ionisation of the air in its path. An example of man-made electrical plasma is the neon sign and its less garish cousin, the fluorescent lamp, both signatures of urban existence.

Sparks that we see some time when an electrical switch is turned off is a transient electrical plasma.

Plasmas used in material processing are usually weakly ionised. The charged particle density is much smaller than the neutral density. The typical degree of ionisation is 10^{-4} to 10^{-6}; that is, one charged particle to 10,000 to a million neutral atoms. This means that the collisions between electrons and neutrals dominate over collisions between electrons and electrons and between electrons and ions.

Charge Neutrality

Though plasma contains electrically charged particles such as electrons and ions, their charges balance on a macroscopic scale. Thus plasma is quasi-neutral. However, microscopically, each particle has an electric field associated with its charge. Each charged particle influences the motion of other charged particles through its electric field; it is this interaction that gives plasma many of its unique properties. This influence falls off inversely as the square of the distance between the interacting particles. Atoms also interact with each other through the electric field, however this decreases as the cube of the distance or even faster. Plasma with its long-range interactions between the particles behaves very much like a fluid.

The propensity of plasmas to maintain charge neutrality can be illustrated by a simple calculation. Imagine that all the electrons in a fluorescent lamp of 1 cm radius is removed leaving only positive ions in the column. The electric field in the radial direction at the wall due to this positive charge will be $ner/2\varepsilon_o$ where n is the ion density (10^{14} /cubic meter, e is the charge $=1.6\text{x}10^{-19}$ Coulombs, r is the radius and ε_o is the dielectric permittivity of free space, which has a value $8.87\text{x } 10^{-12}$ Farads/meter. The actual value can be seen to be close to 100 kV/meter and the potential at the axis of the tube about 1 kilo Volt! Since the plasma electrons in the lamp have an average energy of the order of 1 electron Volt, this charge separation would not be possible spontaneously.

Debye Shielding

By what distance can spontaneous space charge separation take place? We can calculate this by equating the kinetic energy $kT_e/2$ to the potential energy created by charge separation ne^2x^2. This distance of spontaneous charge separation is $\{kT_e / ne^2\}^{1/2}$ and is called the Debye length and has a value $743\{T_e/n\}^{1/2}$. A Debye length is a typical length over which a charged particle's bare electric field has substantial influence. For distances exceeding the Debye length, the electric field of an individual charged particle is effectively shielded out by the surrounding plasma.

The Debye sphere, which is a sphere with radius equal to the Debye length, centred on the charge, is a charged particle's typical "sphere of influence" on neighbouring plasma particles. Not surprisingly, the number of plasma particles that occupy this volume, , plays an important role in defining the Coulomb collisional properties of the plasma and determines the significance of discrete particle effects in general.

Plasma tends to shield out external electric fields imposed at boundaries by a similar process. A charged electrode introduced into the plasma tends to collect a cloud of opposite charge, which insulates the bulk of the plasma from the electrode (fig.2.4). This process was discovered by Debye in electrolytes and is called Debye shielding. This shield of charge is called a sheath and for small applied voltages, the characteristic dimension to which the potential penetrates has a value of the order of few times the Debye length.

It is obvious from the above that a collection of charged particles can be called a plasma only when its dimensional extent well exceeds the Debye length. This can be translated to minimum charged particle density of the order of 10^8 /cc in practical laboratory devices. Below these densities, the collective forces are too weak to keep the particles together. Another criterion relevant to weakly ionised plasmas is that the electron plasma oscillations must exceed the electron neutral collision frequency.

Plasma Potential

The electrons in the plasma, being much lighter than the ions, are quite agile. Their velocity is expressed as $\{kT_e/m\}^{1/2}$ where T_e is the electron temperature in electron volts and m is the mass. For a 1 eV electron, the velocity is typically of the order of 1000 km/sec. A consequence of the high mobility of the electrons is that they escape to the walls in short times. However, the preferential loss of electrons results in the rest of the plasma acquiring a net positive charge, which pulls the electrons back. This ultimately results in a situation where electrons and ions are lost at the same rate, by the establishment of a positive potential well (fig.2.5) trapping the more mobile electrons. The magnitude of this potential is of the order of a few T_e. The plasma thus acquires a potential with respect to the wall, which receives equal fluxes of electrons or ions, or in other words, zero current. Alternately, if we leave a surface exposed to plasma, and leave it floating electrically by collecting no net current, it will attain a negative potential with respect to the plasma.

This self-trapping of the mobile electrons by setting up of a potential has a very important effect on the much less mobile ions. This was discovered by Bohm in 1949 and prescribes the minimum energy with which the ions must enter the sheath. Imagine ions entering the sheath at point A near a negative electrode an arbitrary energy $e\phi$ and a velocity v_i. As the ions get accelerated towards the electrode, their density decreases to keep the flux constant. At point B where the potential is more negative by $\Delta\phi$, the ion velocity would have become $v_i + \Delta v_i$.

The density at B will be: $n_i = n_0 v_i / (v_i + \Delta v_i)$

As point B is more negative with respect to the plasma, the electron density also would have decreased as determined by the Boltzmann equation, i.e. to $n_e = n_o \exp\{-e\Delta\phi / kT_e\}$. The electron density must decrease faster than ion density as we move away from A to enable the formation of the ion rich sheath, $n_i > n_e$

$$\exp\{-e\Delta\phi / kT_e\} < v_i / v_i + \Delta v_i = \{1 - \Delta v_i / v_i\} = 1 - \Delta\phi/2\phi$$

Approximating the left hand side as $1 - e\Delta\phi / kT_e$, for $e\Delta\phi$ much less than kT_e

$$e\Delta\phi / kT_e > \Delta\phi/2\phi \text{ or } \phi > kT_e/2e$$

Hence the existence of an ion rich sheath implies that the ions enter this sheath from the plasma with a velocity $\{kT_e/eM\}^{1/2}$ corresponding to an energy $kT_e/2e$. This velocity is called the Bohm velocity. Since the plasma region is defined as field free, ions would have gained this velocity in the intermediate region connecting the sheath with the plasma. This region is called the presheath.

The consequence of the ion accelerating presheath and the fact that plasma would react against excessive loss of electrons is that the plasma would set up a positive potential with respect to the wall. Ions reach the wall at the Bohm velocity. Electrons reach the wall at its thermal velocity but in reduced number determined by the Boltzmann equation because they have to climb a potential hill. Equating these:

$$n_0 e v_s = n_o \exp\{-eV / kT_e\} v_{th}$$

After substituting for the velocities, this can be shown to be:

$$\phi_p = \frac{kT_e}{e} \text{Ln} \{M/2\pi m\}^{1/2}$$

This potential is called the plasma potential and is the potential that the plasma acquires with respect to the wall because of the faster loss of electrons. For argon ions, with 40 Atomic Mass Units, the logarithmic term yields 4.7. This means that argon ions reaching the sheath with energy of 0.5 kT_e will reach the wall with energy of (4.7 + 0.5) kT_e = 5.2 kT_e.

Plasma Oscillations

The presence of charged particles and their interaction through long-range forces allow plasma to support many types of characteristic oscillations. The electron cloud dispersed among the heavy, less mobile ions, if displaced from the mean position, would be pulled back because of the electric field created by the displacement. However, they tend to overshoot the mean position and oscillate about it (fig.2.6). This oscillation time is of the order of the time to move through the distance of the Debye length, which is λ_D/v and hence the frequency of oscillation is $\{ne^2/m\varepsilon\}^{1/2}$. Under certain conditions, these oscillations can propagate as waves.

The period corresponding to the electron plasma oscillation is the characteristic time in which plasma can respond to external oscillatory fields. Any applied field with a frequency below the plasma frequency can be effectively shielded by the rapid response of the electrons. This is exactly how a metallic conductor shields out electromagnetic waves. Hence for frequencies below the plasma frequency, plasma can be considered as a conductor and for frequencies above this, plasma behaves like a dielectric.

Ions also have a characteristic frequency of oscillation called the ion plasma frequency and is equal to $\{ne^2/M\varepsilon\}^{1/2}$ where M is the mass of the ion.

Electrical Conductivity

In weakly ionised plasmas, application of an electric field will accelerate electrons, and they will move in a direction opposite to the direction of the field. They will lose their momentum when they collide with a neutral atom. On an average they will drift with a constant velocity obtained by the balance of acceleration by the electric field and deceleration by collisions. This behaviour is like electric current in a resistor. The collisions with neutrals provide resistivity to the electron motion.

If the frequency of collision is ν_{en}, the average velocity would be velocity gained in a single collision period $1/\nu_{en}$ under the acceleration eE/m and is equal to $eE/m\nu_{en}$. If the electron density is n, these electrons moving with a velocity would constitute a current per unit area equal to $j = nev = ne^2E/m\nu_{en}$. Comparing this with the Ohm's law, $j = \sigma E$, we can deduce that the electrical conductivity of a weakly ionised plasma is $ne^2/m\nu_{en}$. The numerical value is $2.82\text{x}10^{-4}$ n (cm^{-3})/ ν_{en} (sec^{-1}) Ohm^{-1} cm^{-1}. Electron-electron collisions, though more frequent, do not lead to loss of momentum and hence do not figure in the expression for conductivity. At very high degree of ionisation, typically larger than 10^{-3}, electron-ion collisions determine the conductivity. Fully ionised plasma is as good a conductor as copper.

Electron Energy Distribution

The electron population in the plasma is like a gas. There are processes, which heat this gas, as well as processes by which the electrons lose their energy. Hence the particles will have a range of energies. The nature of the distribution of energy among the electrons is characterised by electron energy distribution function (EEDF). The EEDF specifies the relative number of electrons with each value of energy and is in general a function of position and time. The form of this function results from a balance between electron energisation processes and energy loss processes. EEDF is a fundamental parameter of the plasma, which determines many physical and chemical effects in plasma.

Figure 2.7 shows a schematic illustration of the EEDF. The dashed curve is the Maxwellian energy distribution function, which would be obtained under thermodynamic equilibrium where a state of detailed balancing exists for all processes leading to electron production and all processes leading to their loss. This form of energy distribution has an important property that is depends only on one parameter, the temperature. Unfortunately this condition generally does not exist for most processing plasmas. The existence of internal electric fields energises electrons overpopulating the high-energy region of the distribution, relative to the Maxwellian distribution. Inelastic collisions resulting in electron energy loss truncate the high-energy part. The depopulation of the energetic tail of the electrons due to inelastic collisions is particularly important for molecular gases. Sometimes these processes approximately balance and hence we can assign a temperature to the electron population.

Equilibrium and Non-equilibrium Plasmas

The current passed through the resistive plasma heats it. This Joule heating is because of the fact that electrons gain energy from the electric field and gets randomised by collisions with neutrals. The fraction of energy lost by electrons to the neutral atoms is proportional to the ratio of the electron and atomic mass, which is quite small. As a result, the electrons gain random thermal energy or get heated up. If the gas pressure is very high, electrons collide very frequently with the background neutrals and ions, sharing a part of their energy and making them equally hot. In this case the average fluid temperature will be quite high, in the range of thousands of degrees (Fig.2.8). This is the thermal equilibrium plasma.

As the pressure is decreased, the equilibrium between the electron, ion and neutral fluids is lost, with the result that the electron temperature increases, with the ion and neutral species remaining cold. Hence in low-pressure plasmas where the electron-neutral collisions are not effective in energy equilibration, the electrons have a high temperature compared to the neutrals. Such plasmas are called non-equilibrium plasmas. The thermal energy content of these plasmas is quite low. It is not unusual for a simple laboratory plasma device to have electron temperatures of the order of 50,000 degrees C.

Particle Collisions

When plasma particles approach each other, they begin to interact through short range or long range forces. If some property of the particles such as their trajectory or energy is modified through this interaction, we say that a collision has taken place (fig.2.9). There are two types of collisions, elastic and in elastic. Elastic collisions are like collision between hard spheres where only translational energy exchange takes place. Interparticle collisions provide characteristic times in a plasma called relaxation times.

Quantitative description of the collision process requires the definition of a parameter called the collision cross section denoted by σ. The collision cross section may be interpreted as the effective geometrical blocking area offered by the target particles to the incident particles. The number of collisions in unit time called the collision frequency is obviously the number of particles contained in a tube of area σ and length v if the particle is moving with a velocity v. If the density of the target particles is n_t we get:

$$\nu = n_t \sigma v$$

If there are n_I moving particles in unit volume, the total number of interactions per second is $n_I \nu = n_I n_t \sigma v$ which may be called the reaction rate.

When electrons collide with atoms or molecules elastically, the average fractional energy transferred is only 2m/M. In one second, the energy transferred will be this fractional energy times the number of collisions in a second ν_{en} and hence the characteristic time for energy relaxation is $\tau_E = M/2m\nu_{en}$. This has a value in the range of 10^{-14} to 10^{-7} seconds. Electron-ion and ion-ion collisions are infrequent in weakly ionised plasmas. Electron-electron collisions are interceded by Coulomb interaction and has a value $\tau_{ee} = 4x10^4 T^{3/2}/n$.

Collisions between neutral particles tend to make their temperature equilibrate. If the neutrals have a velocity v_n and the distance between collisions is l, the relaxation time for this equilibration $\tau_{nn} = l/ v_n = 1/ n_n \pi \sigma^2 v_n$. This can range from 10^{-10} to 10^{-6} seconds. Collisions between ions and neutrals also have this range.

Electron-molecule collision cross sections (elastic, momentum transfer and vibrational excitation) in the low energy regime from threshold up to a few electron volts are of critical importance in modelling low temperature plasmas. These cross sections play a critical role in determining electron transport properties, mobilities and electron energy distribution functions.

The second type of collisions called in-elastic collisions are those in which, in addition to the kinetic energy change, there is a modification of the internal energy of the particles. The collisional interaction time between electrons and molecules is the time spent by the electrons in the vicinity of the molecules and can be approximated as $t_c = 2a_0/v_e = 10^{-16}$ to 10^{-15} seconds. The typical vibrational period of a molecule is = $\tau_{vib} = 10^{-14}$ to 10^{-13} sec. Vibrational excitation usually leads to dissociation of the molecules.

Chemical Effects in Plasmas

Electron collisions, with a variety of different species and in a variety of environments, play a key role in creating the energetic species that drive the chemistry in the plasma environment. The environment includes high-density plasmas used in the etching of semiconductor materials and in plasma enhanced chemical vapour deposition, a number of environmental remediation situations such as those driven by secondary electron cascades in mixed radioactive waste or in the plasmas used to destroy undesirable compounds or remediate NO_x.

Electronic collisions are uniquely effective in transferring energy to and from the electronic degrees of freedom of the target atom or molecule. For example, unlike "collisions" with photons, which obey a set of selection rules determined primarily by dipole interactions, collisions with electrons could produce singlet-to-singlet or triplet-to-triplet transitions as frequently as singlet-to-triplet transitions. Electronic collisions do not obey selection rules with regard to singlet-to-triplet excitation because the incident electron can exchange with those of the target and thereby change its spin state. Thus electron impact can excite any dissociative state of a molecule and reduce it to fragments. This is a key mechanism by which radicals and molecular fragments are produced in situations ranging from planetary atmospheres to molecular beam sources for experiments in molecular collisions. Another important process is electron-impact ionisation, the mechanism by which ions are created in any gas discharge system, because it can produce any ionic state of the target.

The important electron-molecule collisions are:

1. Excitation

Electron impact electronic excitation plays a crucial role in molecular plasmas for a number of reasons: it is the main route to electron impact dissociation, electronically excited states are chemically very active, and the process leads to electron cooling. In many cases part of the energy transmitted into excited states will be lost to the plasma by emission of photons.

$e^- + M \rightarrow e^- + M^*$ electronic excitation
$e^- + M(n) \rightarrow e^- + M(n')$ vibrational excitation
$e^- + M(j) \rightarrow e^- + M(j')$ rotational excitation

$e + A \rightarrow A^* + e$

$e + AB \rightarrow 2e + A^+ + B^*$
$AB + AC \rightarrow 2A + C^* + B^+ + e$

2. Dissociation: electron impact dissociation of molecules into radicals is one of the most important steps in plasma processing. The characterisation of how a molecule fragments following electron impact excitation is perhaps the single most important process to understand in modelling low temperature plasma processing and electron-driven environmental chemistries. The dissociation of nitrogen molecules by electron impact occur in two stages, first exciting electronic vibrational states and then leading to their break-up.

$e + N2 \rightarrow N + N + e$

3. Ionisation

Energetic electrons can ionise a neutral molecule by an electron detachment or produce an ion and fragments from a polyatomic molecule like CF4.

$e + A \rightarrow A^+ + 2e$ (electron impact ionisation)
$e + AB_2 \rightarrow 2e + AB + B^*$ (dissociative ionisation and excitation)
$A + A^* \rightarrow A + A + e$ (metastable ionisation)

Internal energy in the form of electronic or vibrational energy of reactants increases the amount of energy available for a reaction between molecules and therefore reduce activation barriers. When the collision partner is ionised, the process is termed Penning ionisation:

$He^* + H_2 \rightarrow H_2^+ + He + e$

4. Recombination

Recombination between electrons and ions is an obvious process of loss of charged particles. The rate of density decay is proportional to the product of electron and ion densities. The proportionality constant is the recombination coefficient β. The typical value of β is 10^{-7} cm^3/sec. This means that plasma of density 10^{10} particles/ cm^3 will decay to 1/10th its starting density in about 10 milliseconds. Recombination can also be through a dissociative process, where a molecular ion and an electron can recombine by:

$A_2^+ + e \rightarrow A + A^*$

giving rise to an excited atom. This coefficient also has a value of the order of 10^{-7} cm^3/sec.

The reaction:

$A^+ + e \rightarrow A + h\nu$

results in the production of photons. This is represented by a recombination coefficient with a value of 10^{-12} cm^3/sec, much smaller than the earlier ones. In a variant of this process, electrons are captured by ions to form exited atoms, which then get de-excited by interaction with electrons, ultimately forming ground state atoms. Radiative recombination is the process by which plasmas emit ultraviolet and visible light.

$A^* + BC \rightarrow ABC$
$A^+ + e \rightarrow A$

5. Attachment: Formation of negative ions by electrons attaching to molecules are important in plasma processing reactors because they often act as the nucleation sites for macroparticles and dust. They can be formed by direct electron attachment or through dissociative attachment. The latter is considered to be more important reaction in plasma processing situations.

$e + A \rightarrow A^-$ (electron attachment)
$e + 2A \rightarrow A^+ + A^- + e$ (dissociative attachment)
$e + AB \rightarrow (AB)^- \rightarrow A^- + B$

6. Charge exchange: collisions resulting in the transfer of charge from the incident ion

$He^+ + Cl^2 \rightarrow He + Cl^+ + Cl$

If the identity of the ions does not change, this process is known as symmetric charge exchange.

7. Surface reactions

$AB + C_{solid} \rightarrow A = BC_{vapour}$ chemical etching
$AB \rightarrow A + B_{solid}$ thin film deposition
$A^+ \rightarrow A + e$ secondary electron emission and Auger electrons

$2A + 2BCD \rightarrow ABC + ABD + CD$

The presence of excited and ionised species in the gas makes a new type of chemistry possible in plasma. Typical plasma chemical reactions are: generation of atoms and radicals, isomerization, elimination of atoms or small groups, dimerization/ polymerisation, chemical sputtering, etching of surfaces and synthesis of materials on surfaces. To illustrate this, a comparison is made below:

Conventional chemistry (0 - 5 eV) Reacting species : M
Photochemistry (0 - 7 eV) Reacting species : M M
Plasma chemistry (0 -) Reacting species : M M M M M

Diffusion of Plasma Particles

The charged particles produced in the plasma can be lost by a variety of processes. In this respect plasma formation resembles a chemical reaction in which ionisation is balanced by losses resulting in equilibrium.

In weakly ionised plasmas, the predominant mechanism of particle loss from the plasma region is by diffusion. Diffusion (fig.2.8) is an example of a random walk process where a particle covers a finite distance in any direction by a series of small random steps. If there is a gradient in the density, the process can lead to a loss of particles down the density gradient. This is governed by Fick's law, which states that the flux of particles is proportional to the density gradient and is a direction opposite to the density gradient. Expressed mathematically,

$nv_d = F = -D\,dn/dx$ where D is the diffusion coefficient expressed in particle /m^2/sec.

Consider an ideal case as shown in the figure, where the density linearly changes to zero in a distance L. The gradient is n/L.

$nv_d = -D\,n/L$ and hence $D = Lv_d$. If the time taken for the particle to leave the system is τ, $v_{d=} L/\tau$ and hence $D = L^2/\tau$. If the diffusion is only by collision between like particles, it is called free diffusion. The diffusion coefficient is approximately given by the expression $D = \lambda^2\nu$ where ν is the frequency of collision between particles and λ is the mean free path between collisions.

In plasma, the flux will be driven not only by collision, but also by the drift of the particles in the electric field set up by the movement of the electrons ahead of the ions. This is represented in figure x. The flux of both ions and electrons must be same to maintain charge neutrality.

$nv_{d=} -D_e n/L+\mu_e nE = -D_i n/L+\mu_I nE$ from which,

$$E = \frac{Di-De}{\mu_e+\mu_I}\,\frac{1}{L}$$

Substituting in the flux equation, $\mu_e = e/m\nu$ and $\mu_i = e/M\nu$

$$nv_{d=} -D_i n/L+\mu_I nE \approx n/L\{D_i+\mu_I\frac{De\,)}{\mu_e} \approx n/L\,Di\,\{1+\mu_I\frac{De\ \}}{\mu_e\,Di} = Di(1+Te/Ti)\,n/L$$

$\approx D_a\, n/L$

Thus the ambipolar diffusion coefficient is larger than the free diffusion coefficient for ions by the electron-ion temperature ratio.

The plasma density in a reactor is a result of the loss processes balancing the production processes. Since the loss is predominantly at surface of the reactor, the balance is strongly determined by the surface to volume ratio. Plasma processing equipment thus becomes extremely geometry dependent.

Plasma in a Magnetic Field

An electron moving with a velocity v in a magnetic field of magnitude B experiences a force of magnitude evB in a direction perpendicular to both the velocity and the magnetic field. The result is that the electron orbit is constrained to become a circle (fig. 2.9) whose radius is obtained by equating the centrifugal force with the Lorentz force due to the magnetic field:

$mv^2/a = evB$ or $a = mv/eB$

The time taken to move over the circumference of the circle of radius a will be $2\pi a/v$ and it's inverse is the frequency of the circular motion given by:

$f = eB/2\pi m$ which is called the cyclotron frequency. The circular motion of the electrons produces a circular current:

$I = ef = e^2 B/2\pi m$

The circular motion of the electron is equivalent to a tiny coil carrying a current, which produces its own magnetic field defined by a magnetic moment

$\mu = \pi a^2 I = mv^2 /2B$.

The direction of the magnetic field generated by the electron current loop is anti-parallel to the applied magnetic field and hence reduces the external magnetic field. This property of the electrons makes them diamagnetic.

A situation often encountered in weakly ionised processing plasmas is that in addition to the magnetic field, an electric field is imposed on the plasma. The electric field may be due to the ambipolar drift or externally imposed. This situation is shown in fig.12.

Electrons will move in the cyclotron orbit around the magnetic field line. Consider the orbit near the point P. The electron is decelerated by the electric field, losing the velocity by a small amount given by: $\delta v = eE\delta t/m$.

This reduction in the velocity reduces the Larmor radius by $\delta a = \delta v/\omega = eE\delta t/m\omega$. Effectively the particle has moved to the new point P’. This has taken place in a time δt and hence the velocity of the translation is $\delta a/ \delta t = eE/m\omega = E/B$. This velocity is called electric field drift velocity. Note that since the particle is moving perpendicular to the electric field, no work is being done on the particle. The electric drift velocity is the same for both electrons and ions.

Plasma Waves

Plasmas, unlike ordinary gases, support a wide variety of wave modes because of the interaction between charged particles. Electric and magnetic fields can represent such wavelike disturbances. The frequency and the wave vector are functionally related to one another by a dispersion relationship. Knowledge of the dispersion characteristics of the propagating waves is certainly necessary for an understanding of the plasma state.

The oscillations at the plasma frequency can propagate as a wave because particles, can penetrate into adjacent (displaced) charge layers because of their random thermal motion. This is the Langmuir wave. It is also known variously as the space charge wave, electron plasma wave or simply the plasma wave. The Langmuir wave is an electrostatic (or longitudinal) wave that propagates only in finite temperature plasma, i.e., one in which there is a finite spread of electron velocities.

The ion-acoustic or ion sound wave is another electrostatic wave occurring in field free plasma. At long wavelengths these waves are approximately dispersionless, propagating with speed, $(kT_e/M_i)^{1/2}$
At shorter wavelengths, i.e., when the wavelength approaches the electron Debye length, the electron shielding of the ion motion becomes less efficient and the wave approaches an ion oscillation (analogous to the electron plasma oscillation above) at the ion plasma frequency

Electromagnetic waves in field-free plasma propagate only for frequencies exceeding the plasma frequency. For frequencies below the plasma frequency, the waves are evanescent. For wave frequencies greatly exceeding the plasma frequency the plasma perturbs the wave only slightly from its vacuum form .

Whistlers are an example of an electromagnetic wave, which may propagate in a plasma in a magnetic field. The electric field for the whistler is right hand elliptically polarised (with respect to the mean magnetic field) in general, reducing to pure circular polarisation when the wave propagates parallel to .

Whistlers are a common phenomenon in our own magnetosphere. They may be excited, for example, when electromagnetic energy from a lightning strike enters a magnetic field line duct (a process, which is more efficient near the magnetic poles). Such electromagnetic energy can be guided along closed magnetic field lines though the enhanced ionisation usually present near such magnetic field ducts. The wave travels along the field line and can be observed at the opposite pole (conjugate point). Because the wave is highly dispersive (see above) different frequencies arrive at the conjugate point at different times and, using a radio receiver, a descending glide tone can be heard for each lightning strike occurring in the opposite hemisphere.

At frequencies below the ion cyclotron frequency a

dispersionless (at long wavelength) electromagnetic wave can propagate. This is a magnetohydrodynamic wave called the Alfvén wave. The phase velocity of the wave satisfies
where is the permeability of free space.

Instabilities

Non-linear systems like plasmas are susceptible to various instabilities. In fact the initial phase of the electrical breakdown of the gas and the formation of the plasma can be viewed as an instability. When the space charge field of the initial phase of ionisation exceeds a threshold, it begins to be shielded from the bulk of the plasma. This localisation of the field increases the flux of ions falling on the cathode, causing increased secondary electron emission, which produces more ionisation enhancing the shielding effect further. Events connecting electron emission-ionisation-shielding-sheath contraction-ion flux increase-secondary electron production cycle thus grows by positive feedback eventually stabilising at some equilibrium plasma density, characteristic of the fully grown discharge.

Most plasmas have inherent non-uniformity in both density and particle energy distributions. The collisional processes through diffusion will smooth such density gradients. However, these, being away from equilibrium, can be viewed as sources of free energy, which can create internal electric and magnetic fields. These in turn interact with plasma parameters in a non-linear manner. The characteristic waves of the plasma can be amplified by interaction with these electric and magnetic fields and can grow to large amplitudes. These overgrown waves are called instabilities. The ultimate effects of these waves will be to smooth the inhomogeneities and anisotropies in times faster than the collisional smoothening.

The glow discharge plasmas used in the plasma processing context, are weakly ionised collisional plasmas and are prone to instabilities related to non-linear coupling between electron temperature and ionisation and attachment rate coefficients. Spatial modulation density in glow discharges called striations (fig.13) is an example. The instabilities appear as current and power modulation and oscillations in plasma density and temperature. The higher density, less collisional ECR plasmas have instabilities which appear either as mod-hops related to coupling between propagating electromagnetic waves and non-uniformity in plasma density and magnetic fields and results in time dependence of the coupled power and resultant modulation of plasma parameters.

Macroparticles in Plasmas

Industrial plasmas often contain macroscopic dust particles. Dust as a contaminant in processing plasmas can originate from plasma chemical synthesis in the gas phase, e.g. silicon from silane or from sputtering from electrodes. Equilibrium vapour pressure of these metals is very small and hence the metal vapour exists in supersaturated state and can form clusters very rapidly. The early growth rates are very fast, experiments show 100 nm particles forming in 1 μsec. Negative ions appear necessary as a nucleation centre. A negative ion become a cluster and achieves macroscopic character at a critical dimension at 10^{-7} cm. In order to stay at the floating potential, the dust must acquire negative charge, but not so much that the radial electric stress exceed the tensile strength of the material.

Radiation from Plasma

Plasmas are excellent sources of radiation, which can be of atomic or collective in origin. Electrons gain energy from the electric field and lose most of that energy to inelastic collisions exciting atomic levels which radiate light. Desired spectrum can be tuned by combining different gases in the plasma, for example the 254-nm emission in the mercury-argon mixture in the fluorescent lamp. Arc plasma sources can radiate up to fifty percent of its energy. Plasmas also emit continuum radiation by collective processes. Electrons interacting with the electric field of neighbouring particles emit bremsstrahlung radiation. Continuous acceleration of electrons gyrating around magnetic field lines also gives rise to radiation http://physics

Fundamental plasma descriptions

Ordinary gas made up of neutral particles obeys the laws of kinetic theory. Particles interact only through direct collisions and are otherwise unaffected by each other. In plasma, however, the Coulomb force experienced by each particle is due to the electric field produced by all particles over long spatial scale lengths. The long-range nature of the electro-magnetic interaction introduces many-body correlation effects and renders the problem intractable beyond the smallest numbers of particles without simplifications of some kind.

Broadly speaking however, there are three representations, which capture the essence plasma behaviour on different temporal and spatial scales, each with its own strengths and weaknesses.

The first is the so-called single particle theory, which describes the behaviour of individual particles in electric and magnetic fields. The particle trajectories are computed under the influence of the Lorentz force exerted by the local electric and magnetic fields. This method provides much useful insight into the dynamics of isolated particles. Concept of particle drifts is a very useful result. This method does not attempt to deal with realistic ensembles of particles and the electric field is thus treated in an *ad hoc* fashion.

The second approach is a very fundamental description of the plasma state, known as kinetic theory. It essentially consists of a Newtonian-type description of the many body system in the presence of electromagnetic fields. A 6-dimensional distribution function is defined for each plasma species , which is the number of particles in the volume element with position and the velocity at any time.

Stipulating conservation of each particle type in phase space leads to kinetic equations, the moments of which give a modified set of multi-fluid equations, which incorporate the electromagnetic forces. In the fluid framework, the variables are more experimentally accessible: e.g., the number density, fluid velocity and pressure of a plasma species. The theory is complex and suffers from the drawback of requiring artificial closure of the moment equations, but deals with a very broad range of phenomena. Indeed many important plasma phenomena, such as Landau damping can only be understood properly using such a model. Its application is usually limited to simple geometries or where the assumption of a leading order Maxwellian distribution function is valid.

The third means is to simplify the multi-fluid model by summing over the plasma species whilst incorporating approximations such as neglecting the small electron mass (compared with that of the ion species) and the Maxwell displacement current. This yields a greatly simplified single-fluid picture of the plasma.

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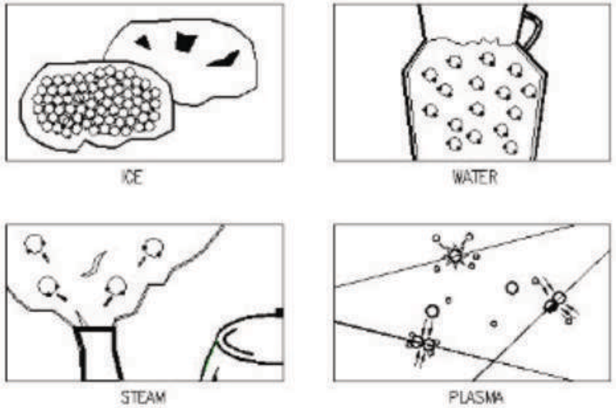


Fig.2.1. When a gas is heated to very high temperatures, or when subjected to energetic radiation, the atoms dissociate into electrons and ions and form plasma

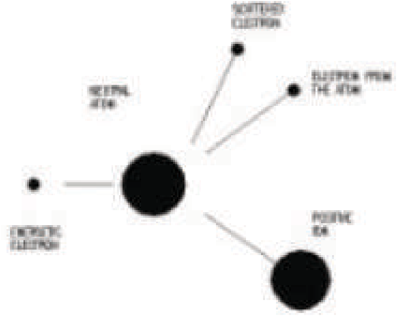


Fig. 2.2. Ionisation is the process of separating electrons from the nuclei to which they are bound.

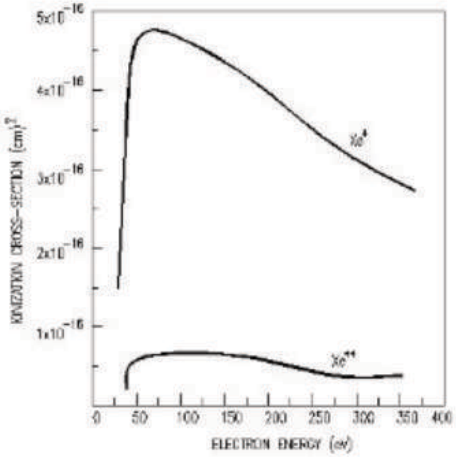


Fig. 2.3. The electron impact ionisation for most atoms has a cross-section of 10^{-16} cm^2 when the ionising electron has an energy of about 100 electron volts

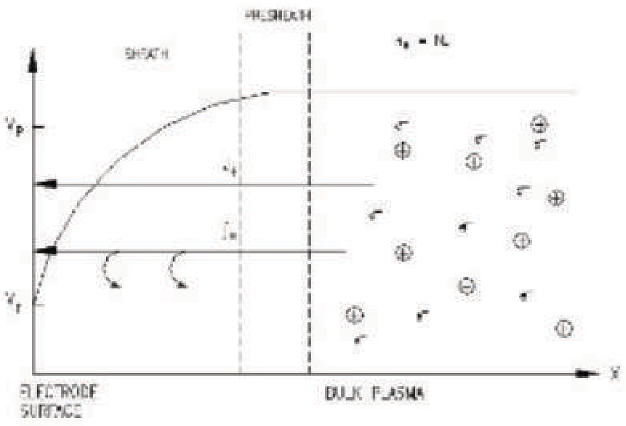


Fig. 2.4. Plasma shields out external electric fields. A charged electrode introduced into the plasma tends to collect a cloud of opposite charge, which insulates the bulk of the plasma from the electrode

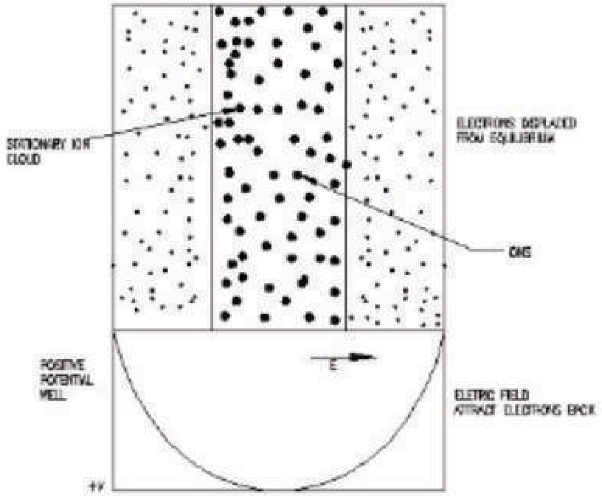


Fig. 2.5. Escape of highly mobile electrons to the walls make the plasma acquire positive potential and ultimately results in a situation where electrons and ions are lost at the same rate

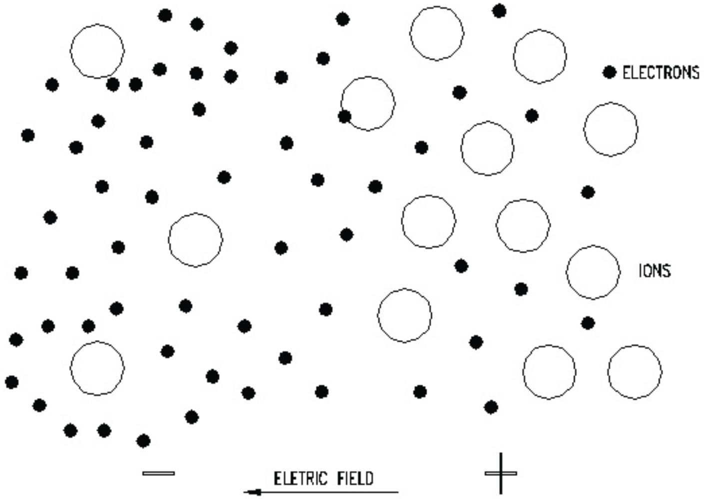
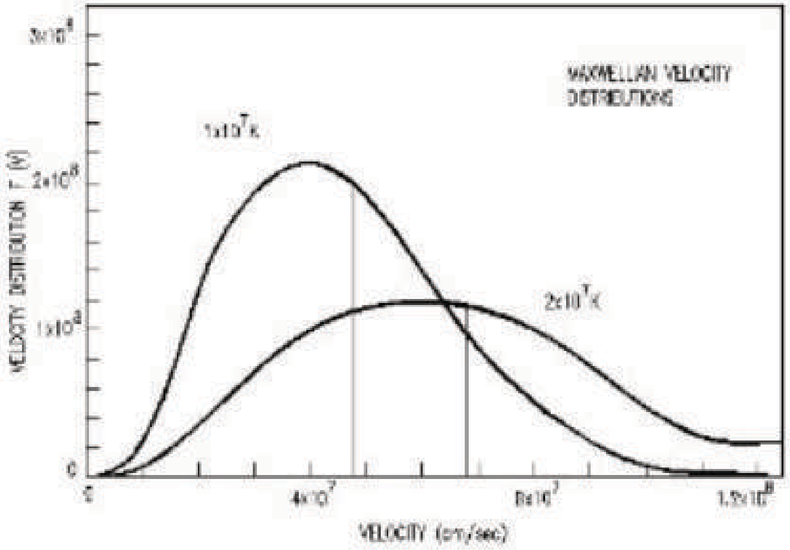
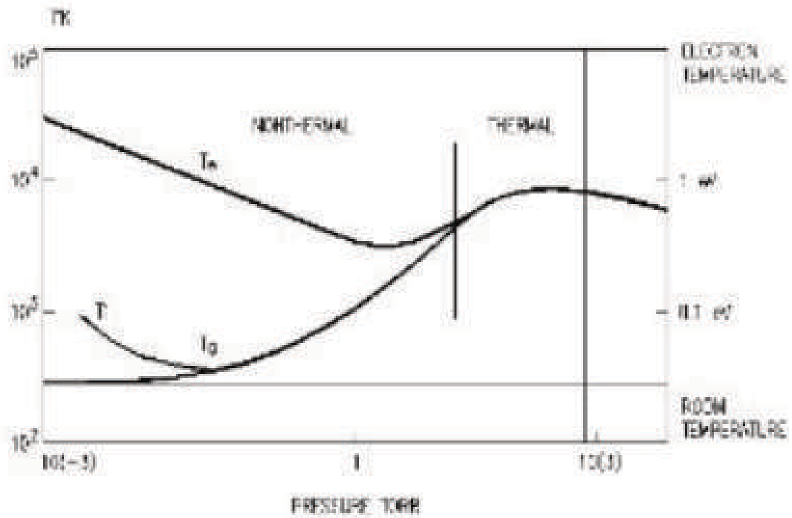


Fig. 2.6. The electron cloud dispersed among the heavy, less mobile
[illegible] acteristic





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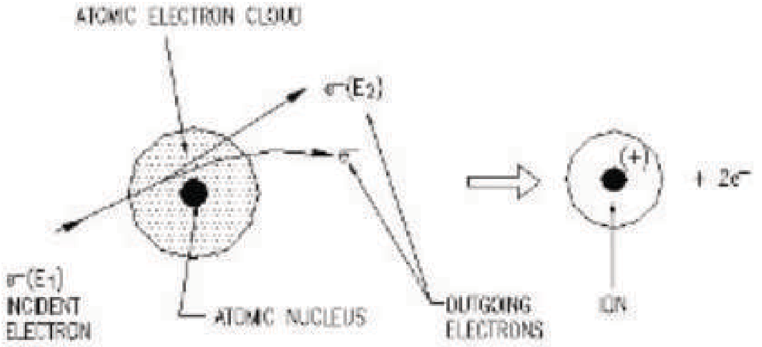
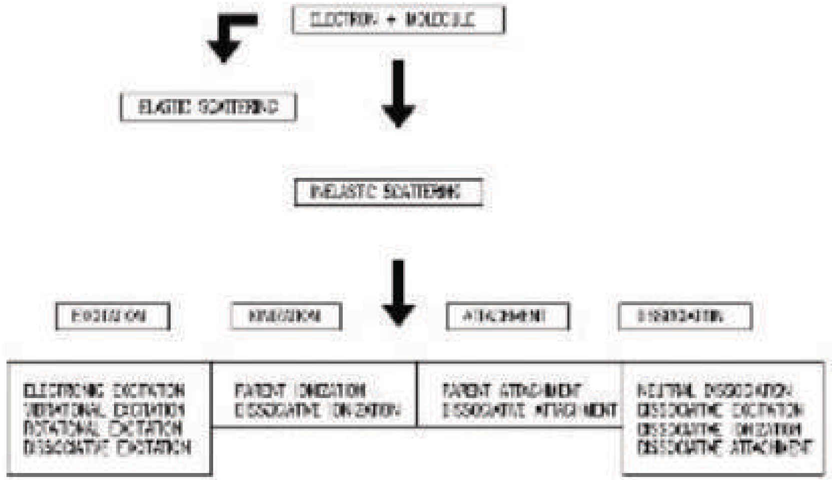


Fig. 2.9. If some property of the particles such as their trajectory or energy is modified through an interaction, we say that a collision has taken place



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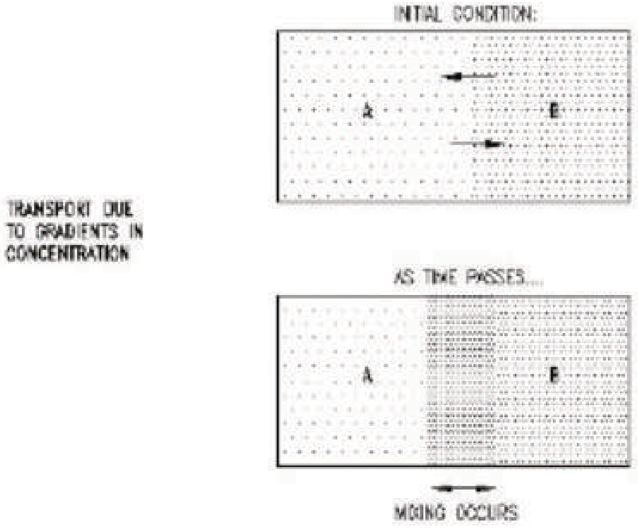

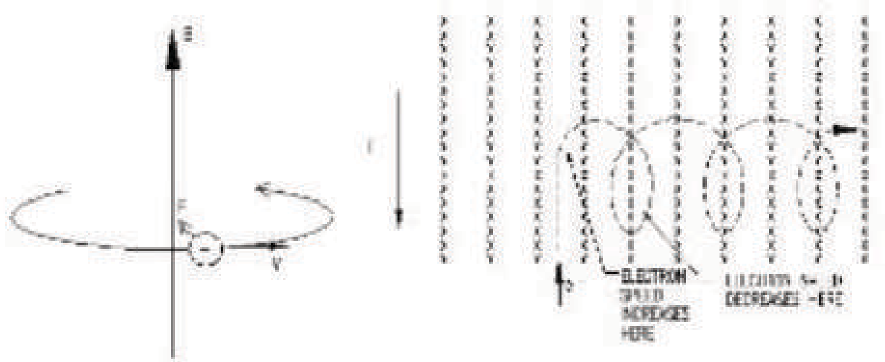

Fig. 2.12. (a) In a magnetic field, the electron orbit is constrained to become a circle whose radius is obtained by equating the centrifugal force with the Lorentz force. (b) An electric field perpendicular to a magnetic field will make the electrons drift in a direction perpendicular to both

3. Taming the Lightning

Plasma Sources in the Laboratory

Industrial plasma sources use electrical breakdown of the gas to produce plasma. This technology can be traced back to studies on gas discharge physics in the late 19th century and the early 20th century. A large variety of plasma sources have been developed over the years for various applications. They differ from each other by the means energising the electrons, how they partition their energy to the plasma particles, and how the plasma formed reacts back on the power source and the dominant loss process. In this chapter, we shall discuss some generic varieties in some detail.

Electron Impact Ionisation

An electron may form a positive ion by collision with an atom or molecule, provided its initial kinetic energy is in excess of the threshold energy for ionisation. This can be represented as:

$$e + H = H^{+} + 2e$$

The rate of this process is proportional to the ionisation frequency , or the number of ionisation events created by an electron in one second. The ionisation probability is characterised by the cross section for ionisation and depends on the kinetic energy of the electron and the internal characteristics of the atom. The cross section for electron impact ionisation rises steeply from zero at the threshold to a maximum of the order of $10^{-16}\ cm^{2}$ at an energy between three and six times the ionisation potential and falls off approximately exponentially with an e-folding energy of 500 eV. Ionisation by electrons in the 100 eV energy range (fig 3.1) is thus rather efficient. Hence most plasma devices depend on electron impact ionisation to produce plasmas.

Electrical Breakdown

Townsend's early experiments-circa 1914-with currents in discharge tubes created by dc potentials on the electrodes brought out an anomalous behaviour. The current was found to increase with increasing electrode separation. His explanation laid the foundation of electrical breakdown of gases.

The mechanism of electrical breakdown is schematically shown in fig 3.2. Imagine two parallel plates with a separation of d and voltage of V. The electrons liberated from the cathode due to some process are accelerated by the electric field and ionise new molecules. The new electrons also accelerate and take part in ionisation. The overall effect is that the electron density in the column increases exponentially along the distance traversed by the electrons. This process is called an avalanche.

Each ionisation event produces a positive ion also. These positive ions are also accelerated and are attracted towards the cathode. Each positive ion falling on the cathode liberates new □electrons by secondary emission process. If this number is equal to the initiating number of electrons we have a self-sustaining discharge situation. This condition, known as the Townsend condition, can be written as:

$$\gamma\ \exp(\alpha d) = 1$$

By definition, $N_g\ v_e/v_d$ where v_e is the average ionisation rate and v_d is the drift velocity of electrons under the electric field.

Electrical breakdown is a process dependent upon many variables. In such situations, similarity principles are invoked understand the quantitative relationship between different variables. Townsend obtained a semi-empirical relationship defining the above as:

$\alpha = A\ p\ \exp\{-Bp/E\}$, where A and B are constants. It is useful to remember that for air at relatively high E/p value, $1.17 \times 10^{-4}\ p\ cm^{-1}$ where p is in Torr.

Combining this with the Townsend condition:

$$Bp/E = \mathrm{Ln}\ (Apd)\ \mathrm{Ln}\ \mathrm{Ln}\ (1/\gamma)$$

Using the fact that E = V/d

$$V_b = Bpd / \mathrm{Ln}\ (Apd) - \mathrm{Ln}\ \mathrm{Ln}\ (1/\gamma)$$

This is the breakdown condition relating the voltage for breakdown of the gas to the pressure and the electrode separation.

This equation, when plotted in a graph between V_b and pd gives the Paschen curve (fig.3.3) showing that there is a minimum voltage for the breakdown of a gap. The physical reason for the minimum is that at low value of pd, there are not enough ionising collisions, while at high values of pd, electrons do not gain enough energy between collisions for ionisation.

In order to create one electron-ion pair, it must be accelerated to energy $W = eE/$□. Even under the most favourable conditions the creation of an electron-ion pair consumes energy, which is several times the ionisation potential. In air, W=66eV/pair.

2. DC Glow Discharge

If the voltage is above what is required to drive the Townsend discharge, the ionisation process can take the form of an avalanche with the newly created electrons gaining energy from the field and producing new electron-ion pairs. This process of build up of free electrons is supported by the release of electrons from the cathode by the energetic ions falling on it and releasing secondary electrons. In a short time, the column will have built up sufficient plasma density such that the bulk of the column cannot sustain the electric field because the highly mobile electrons would equalise the potential. This results in the exclusion of the applied field to the boundaries of the plasma, which are the electrodes. This is the state of a fully developed dc electrical discharge.

The sustaining process of the dc discharge is the release of secondary electrons from the cathode. This is facilitated by the ion neutralisation by recombination at the cathode surface. In some of these reactions, one electron enters the ground state of the atom and the excess energy leads to the release of a second electron from the solid. This process is the Auger emission or more familiarly, the secondary electron emission. The process is usually characterised by the secondary emission coefficient. To facilitate secondary emission, the ions falling into the anode from the plasma must have high enough kinetic energy to release sufficient number of secondary electrons. This is the basic reason for the relatively high voltages required sustaining the glow discharge. The ion concentration at the cathode fortuitously provide the ion sheath near the cathode which, being resistive, provide the potential difference for ion acceleration.

Features of a Glow Discharge

The general behaviour of a dc discharge can be represented in terms of their voltage current relationship shown in fig.3.4. The way this figure is obtained is also shown in the circuit diagram in the figure, where a power supply is connected in series with an evacuated discharge tube and a variable resistance. The resistance is much larger than the impedance of the discharge and hence by varying its value, any arbitrary current can be drawn from the power supply. The corresponding voltage is then plotted.

The electrical breakdown happens when the applied voltage exceeds some critical value. The current density is of the order of microampere per square cm. By adjusting the external resistance, the discharge can made to enter a region where the voltage does not substantially change. There is in fact a slight a slight decrease of voltage as the current increases, which is attributed to gas heating. This is the region of normal glow discharge and is characterised a visible glow around parts of the cathode. The current density is typically less than a milliampere per square cm and is constant for a pressure and electrode material. Further increase in current makes the discharge cover larger and larger area of the cathode until the entire the cathode area is immersed in the discharge. The region of positive increase in voltage with current is the abnormal glow or anomalous glow.

Glow discharge plasmas have certain generic features (fig.3.5), which are easy to distinguish. Near the cathode, there are relatively dark regions called Aston and Crooke’s dark space, which are identical to the cathode sheath where most of the voltage applied between the cathode and the anode appears. The electrons originating from the cathode are accelerated in this region. Beyond this is a region of intense brightness, where these electrons ionise the gas, which emit the characteristic spectral colour of the gas. The negative glow region merges into the positive column, which is the quasineutral plasma region of low electric field. The positive column connects to the anode through the anode glow and the anode dark space. The anode glow can be uniform across the anode surface or can be spots of luminous spheres on the anode surface.

DC glow discharge plasma devices have been popular in plasma processing applications because of their intrinsic simplicity and wide operating range. It is extensively used in thin film deposition, plasma diffusion treatments and plasma chemistry. The electron temperature is determined by the balance between power dissipated in the discharge and power loss to the walls through the drift of charged particles [a]. The electron density in a glow discharge is of the order of 10^8 to 10^{11} cm^{-3}, for pressures in the Torr range. At this pressure the neutral density is in the range of 10^{16} to 10^{17} cm^{-3}. The electron temperatures are in the range of

1-3 eV, which corresponds to thermodynamically equilibrium ionisation of 10^{-2} or higher. The actual degree of ionisation of the gas is 10^{-8} to 10^{-7}. This disparity is because the glow discharge is a non-equilibrium phenomenon where the ionisation is not balanced by radiative recombination.

Glow Discharge Instabilities

Glow discharges are susceptible to instabilities. The most common instability results in periodic structures of high and low density regions, which move from the anode to the cathode with velocities of the order of 100 m/s. Another common instability is due to local heating of the gas by the discharge. Any localised inhomogeneity in density results in increased power deposition, increasing the gas temperature, which decreases the gas density. Higher E/p increases the local electron temperature, which results in increased ionisation and density increase. Thus, the chain of events builds up through the feedback mechanism of electron temperature dependence of the ionisation rate. This can ultimately result in an initially diffuse and uniform plasma column getting transformed to a filamented one.

Corona and Dielectric Barrier Discharges

Two variants of glow discharges may be mentioned here briefly. Corona is a self-sustained low current glow discharge in highly non-uniform electric field (fig.3.6). Such electric fields can be generated around thin wires or sharp needles. The primary ionisation processes are confined to the high field region. The plasma formed around the electrode shields the applied electric field stopping the discharge transiently. Clearing of the space charge start the process again. Thus, the corona current is composed on highly repetitive nanosecond pulses.

Dielectric barrier discharges are similar to glow discharges except for the presence of a dielectric layer at the electrode. When ac voltage is applied to the electrodes, the dielectric barrier prevents glow to arc transition and lead to the formation of a large number of microdischarges randomly distributed in space and time. Dielectric barrier or Silent Discharges are extensively used in ozone production and flue gas treatment.

3. Intensified Glow Discharges

The ordinary glow discharges are usually limited to operation at low degree of ionisation, primarily because the ionising electrons are not efficiently used. The efficiency of glow discharge can be substantially improved if the primarily electrons are trapped in the volume and their ionisation collisions increased. There are two approaches to this: electrostatic trapping and magnetic trapping. We will discuss a few configurations of intensified glow discharges.

Hollow Cathode Glow Discharge

In the hollow cathode discharge, the cathode has a closed geometry like a single or multiple pipes or closely kept parallel plates [d]. The electrons emitted are trapped within the cathode (fig.3.7), intensifying the plasma density by orders of magnitude. The most important feature of the hollow cathode discharge (HCD) is known as the hollow cathode effect. In the HCD, the fast electrons are electrostatically confined and can oscillate between opposing cathode surfaces. These electrons are called pendular electrons. This trapping makes the electrons dissipate the energy acquired from the cathode very efficiency. This enhances the plasma density and the ion flux to the cathode to produce secondary emission in increased. The combination of these effects results in enhanced density of the HCD, which is sensitive to its geometry.

Typically, these discharges are operated at subtorr pressures and the cathode hole diameters in the centimetre range. The lower limit is pressure is determined by the loss of Pendel electrons from the discharge and is empirically given by

$Pd = Ln\,(f^{-1})/n$ where n is the gas density at 1 torr pressure and is the average collision cross section.

Penning Discharge

Penning discovered that ionising electrons could be trapped between negative electrodes using an axial magnetic field (see fig. 3.8). Plasma ions would be lost to the cathodes while the electrons would diffuse ambipolarly to the walls in the radial direction. The trapped electrons would thus take part in ionising collisions efficiently and the density enhancement can be substantial. Because of the reflected trajectory of primary electrons these discharges are also known as reflex discharges.

The radial electric field is developed because of the magnetic insulation of electron diffusion. The electrons execute cross-field rotation under the ExB action. This is the basis of the magnetron discharges extensively used in sputtering and film deposition applications.

The electron confinement on a magnetron is due to the presence of orthogonal E and B fields at the cathode surface. This results in a classic E x B drift for electrons (the Hall effect), which gives rise to a sequence of cycloidal hopping steps parallel to the cathode face (Figure 3.9). As a result, the secondary electrons, which are emitted from the cathode because of ion bombardment, are confined to the near vicinity of the cathode. In a magnetron, the electric field is always oriented normal to the surface of the cathode. The transverse magnetic field is configured so that the E x B drift paths form closed loops, in which the trapped, drifting electrons are constrained to circulate many times around the cathode face.

The most common design for a magnetron cathode is the circular planar cathode, in which the cathode is simply a flat, circular disk, and the E x B drift currents form circles centred on the disk axis, around the face of the cathode. The magnitude of the total drift current can be measured by means of its induced magnetic field, and results indicate a ratio of about 3-7 for the circulating current compared to the discharge, or net current [2]. On average, this ratio is a measure of the trapping and the number of times a secondary electron traverses the E x B drift loop prior to leaving the discharge and arriving at the anode. This ratio indicates the length of the drift path for the electrons. This allows the data to be scaled to larger cathodes or ones with differing E x B paths.

4. Arc Discharge

Glow to Arc Transition

Beyond the abnormal glow discharge region of voltage increase with current, the discharge has a tendency to slide into a region of abrupt current increase and voltage drop. This is called the glow to arc transition. Either an increase of the discharge current or the gas pressure or both can cause the transition. Though glow discharges and arc discharges are fundamentally similar in the sense that both are maintained by ionisation of the bulk gas by electrons emitted from the cathode and energised by the inter-electrode voltage, a number of features distinguish the arc discharge from glow discharges.

The localised heating of the cathode to high temperatures ensures electron emission from the cathode through mechanisms other than the secondary emission of electrons, which was the sustaining process of glow discharges.

Electron Emission Mechanisms

This localised electron emission happens in three characteristic modes. In the diffuse attachment or spot mode of the current, the electron emission is by a process identical to what happens in vacuum tubes with heated cathodes. This is the thermionic emission process in which the electrons in the conduction band of the metal are, so to say, boiled off at high temperatures. This follows a rule first enunciated by Richardson, which relates the emission current density to the temperature in the following way:

$$J_c = A_c T^2 \exp \{-e_w/kT\}$$

$_w$ is called the work function of the metal and is defined as the energy required by the electrons to escape from the metal. A_c is a constant numerically equal to 1.2×10^6 / m^2/degree K. At temperatures more than 3500 degrees the current density is in the range of 100 to 10,000 A/cm^2. This mode of arc discharge is possible in carbon and refractory metals such as tungsten, molybdenum, tantalum etc. which can withstand such high temperatures without melting. For such metals the equilibrium thermionic electron flux is greater than the flux of neutral atoms. Tungsten is a favourite cathode material since the melting temperature is 3700^o K and the boiling point is 5900^oK. The emission spot is stationary or relatively slow moving.

Thermionic emission is the escape of electrons from a heated surface. Electrons are effectively evaporated from the material. To escape from the metal, electrons must have a component of velocity at right angles to the surface and their corresponding kinetic energy must be at least equal to the work done in passing through the surface [24]. This minimum energy is known as the 'work function'. If the heated surface forms a cathode, then at a given temperature T (° K) the maximum current density emitted is given by the Richardson-Dushman equation: -

$$J = A.\ T^2.\ e^{(-11600.\ \Phi\ /\ T)}$$

Where Φ is the work function (eV) and A is a constant with a theoretical value of 120 A/cm^2. K. In reality this value is not attained for real materials. Table 3 illustrates the basic characteristics of some thermionic emitter materials that are commonly used. It can be seen that the most important parameter for thermionic emission is that the work function as should be as low as possible to use a cathode at an acceptable temperature. The mixed oxide cathode is commonly found in small radio type valves. Cs/W/O, although not good for thermal emitters, is usually found in phototubes whilst the heavy metal cathodes are used in high power electron tube devices.

Thermionic cathode arcs can be maintained with cathodes heated with external sources. Activated cathodes can also bring down the required temperature for electron emission. Arcs of this type are generally used in low-pressure discharges where the cathode current densities are low to produce self-heating of the cathode.

Table 3

Important characteristics of some thermionic emitter materials

<TBODY>Material		A		Temp (° K)	J (A/cm²)
Tungsten	60	4.54	2500	0.3	
Thoriated W	3	2.63	1900	1.16	
Mixed oxides	0.01	1.	1200	1.	
Caesium	162	1.81			
Tantalum	60	3.38	2500	2.38	
Cs/O/W	0.003	0.72	1000	0.35 </TBODY>	

In a diode structure, electrons leaving the cathode surface lower the electric field at the surface. A stable condition exists when the field is zero as any further reduction would repel electrons back to the cathode. This stable regime is known as 'space-charge-limited emission' and is governed by the Child Langmuir equation: -

$$J = P.\ V^{3/2}$$

where P, a constant which is a function of the geometry of the system, is known as the perveance. However, if the voltage becomes sufficiently high, the Richardson limit for current is reached when the emission becomes temperature limited. Figure 15 shows the characteristics of an ideal diode.

The second mode of electron emission and generally occurring in a second group of metals like aluminium, chromium, copper etc. is through a single or multiple spot rapidly moving on the surface. Local hot spots appear and disappear and move on the cathode surface randomly. Temperatures are of the order of 3000 degrees or less while the current densities a of the order of 10^4-10^8 Amp/cm$^{2.}$ Hence it is postulated that Field emission in conjunction with thermionic emission (sometimes called thermionic field emission) is responsible for electron emission. These metals also have the property of releasing metal vapour and plasma jets. High current, low voltage arcs can be sustained in the metal vapour of these materials.

The application of a high voltage between a fine point cathode and a contra surface can, by a tunnelling effect, give sufficient energy to an electron so that it escapes from the surface. This phenomenon is known as high-field or Fowler-Nordheim emission. It should not be forgotten that the electric field around a point is greatly enhanced relative to the apparent average electric field between the electrodes. The current density (A/m^2) emitted by such a point is given by: -

$$J = (1.54.\ 10^{-10}.\ E2\ /\ \Phi\ ).\ e^{(-6.83*109\ .\ 3/2\ .\ k\ /\ E)}$$

Where E is the electric field at the emitter, Φ the work function and k a constant approximately equal to 1.

With fields of the order of 10^9V/m, current densities can attain 10^{12} A/m^2 but the actual current is quite small due to the small surface of the emitter. More reasonable currents can be obtained by multiplying the emitter sites. Needles or razor blades can be used as emitter arrays and arrays etched in silicon have shown some success in electron tubes. The major disadvantage of this type of source is that an excessive current density can destroy the points either by erosion or self heating.

Mesyats discovered A third mode of cathode operation in 1966. If a very high voltage pulse of short duration in tens of nanoseconds is applied to the cathode, field emission starts on the microscopic protrusion called whiskers on the cathode surface. The intense localisation of ohmic heating on the whisker make them evaporate and a very high-density plasma layer is formed on the surface of the cathode. This plasma layer can then start electron emission with current densities of the order of 10^8 to 10^9 A/cm^2.

Cathode Sheath

Electrons emitted from the cathode and traversing the arc column towards the anode gain energy from the electric field in the cathode fall as in the case of the glow discharge (fig.3.10). The ions produced by the electrons gain energy from the cathode fall and carry it to the cathode where it is released by neutralisation. The major feature distinguishing the arcs from glow discharges is the magnitude of the cathode potential drop which is of the order of the ionisation potential of the gas; typically, 10-30 volts. This is because the requirement of secondary electron production by energetic ions is not needed to sustain the arc.

The electrons accelerated though the cathode sheath loses energy to ions and neutrals by collisions. At high enough pressures the plasma constituents are in equilibrium, resulting in the generation of a hot (~5000-10000 degrees) plasma in the arc column. This is also a feature different from the glow discharge plasmas, which are generally not in equilibrium. **Maecker Effect**

High current arcs are characterised by strong macroscopic flows induced by the arc itself [a]. Any variation of the current carrying cross section of the column leads to induced flows [b]. The current generates an azimuthal magnetic field, which produces a magnetohydrodynamic pinch of the plasma, and in equilibrium, the plasma pressure balances this pinch through:

$$J \times B = \text{grad } p$$

As the plasma spreads out radially from the cathode, the radial component of the current, interacting with the azimuthal magnetic field, produces an axial acceleration of the plasma. This can result in streaming velocities of the order of 100 m/sec. This is the Maecker effect resulting in the aspiration of the plasma generating gas into the plasma column by the magnetohydrodynamic pumping.

Entrainment and Diffusion Effects

Arc plasmas diffuse through the ambipolar diffusion mechanism. Another diffusional effect called demixing is important when the plasma column consist of two gases, a situation common in processing applications. Atomic gases tend to concentrate in the hot interior of the plasma while molecular gases diffuse to the outer, cooler regions. Similarly, gases with higher ionisation potential concentrate at the axis. Plasma in SF_6 commonly used in circuit breakers show a concentration ratio of fluorine at the axis to sulphur at the edge of 20. Similarly, metal vapours will concentrate at the edge of the arc plasma.

Heat Transfer to the Anode

The anode absorbs electrons. This mode of heat transfer to the anode can be as high as 80 to 90 per cent of the electrical energy deposited into the column. This region can be divided into several zones. The flow affected zone followed towards the anode by a layer in which the presence of the relatively cold anode is felt and which is characterised by the steep gradients in temperature and particle densities. This layer is called the boundary layer. At the bottom of the boundary layer is the anode sheath. The location of the current transfer to the anode is called anode arc root. If this is diffuse, the anode fall is negative while in the case of a constricted anode root, the fall may be positive [c].

The second mode of heat loss in arcs is by radiation from the column. The radiation has thermal and recombination components and it is proportional to the square of the density approximately. Radiation loss can be very high in high-pressure arcs, approaching 90 per cent. This is the basis of high power arc lamps. The gas flow has another function. It stabilises the arc and also is designed to align it to a narrow column. This aligned flow, striking the anode can deposit energy in concentrated manner resulting in rapid melting and vaporisation.

5. Vacuum Arcs

Metals can be divided into two groups [2] with respect to their thermionic emission properties. The first group contains the refractory metals: tungsten, molybdenum, tantalum etc. for which the equilibrium thermionic electron flux is greater than the flux of neutral atoms. The second group of metals like aluminium, chromium, copper etc. generates large thermal flux of vapour on heating. High current, low voltage arc discharges can be sustained in the metal vapour of these materials. These arcs are called vacuum arcs.

Vacuum Arc Phenomenology

Surface of metals usually contains micron-sized protrusions called whiskers. Field emission (electric fields ~ 10^{10} V/m and current densities ~ 10^8 - 10^{11} A/m^2) from the whiskers can heat them to temperatures in excess of the boiling point in times shorter than one nanosecond. The supercritical fluid thus formed may have pressures of the order of 10^{10} Pa. and emits electrons by a combination of thermionic and field emission mechanisms. The emitted electrons are collisionally accelerated and ionise the evaporated metal vapour (Fig.3.11). Pressure ionisation is also invoked. The plasma undergoes explosive expansion [4], by some complex process involving pressure and electrostatic forces. The positive space charge forms a potential hump and the ions formed in the region are accelerated in two directions; back to the cathode to sustain the discharge and away from the cathode by the repulsion by the hump as well as plasma expansion. Finally, each cathode spot produces highly ionised high-energy plasma jet with an ion current component of about 7-12 % of the total arc current. These fluxes of plasma contain electrons, singly and multiply ionised ions, atoms and macroparticles. Redeposition of energy continues the process, with rapid movement of the location of the cathode spot, with velocities of the order of 1-100 m/s. Thus, the cathodic arc is in fact a series of micro arcs meandering to regions neighbouring the preceding arc.

Arc Root Dynamics

The arc root is neutrally stable to motion across the cathode surface and hence wanders on the surface. Some experiments indicate that there are two time scales [5] for the random motion: a very short spot residence time of tens of nanoseconds and a longer time scale of 100 microseconds, both of which have different diffusion constants associated with them. With increasing time, the spot motion also slows down, sometime becoming stationary for tens of microseconds. Local surface temperature change due to local heat accumulation has been attributed to this

Imposing a magnetic field parallel to the surface restores control. The arc spot now moves in the -JxB direction with the trajectory preferring regions where the magnetic field is parallel to the surface. A number of models have tried to explain this anti-Amperian motion of the vacuum arc. The two relatively successful models are due to Schrade (6) and Harris (7). Schrade finds that the current carrying arc is unstable to small deviations from the perpendicular and that it bends towards the -JxB until it touches the cathode surface and initiates a new arc. In Harris's model, the arc plasma is a disc with excess of positive charge situated above the cathode surface. The differential displacement of electrons and ions due to vxB force produces excess positive charge on the retrograde direction and negative charge on the JxB direction. The excess negative charge inhibits electron emission from the cathode while the excess positive charge increases it, making the arc to re-strike on the -JxB side.

A notable feature of the vacuum arc is that it produces ions with energies exceeding the cathode-anode voltage. There are a number of theories (8) describing the arc spot phenomena responsible for the hike in energy. The potential hump theory proposes excess positive space charge accumulation near the cathode resulting in a virtual anode formation leading to ion acceleration to energies exceeding the applied voltage difference. The gas dynamic theory states that the momentum transferred to the ions from the arc electron flux through collisions is responsible for the excess energy. Experimentally the ion energy distribution seems to fall between the two predictions indicating both mechanisms to be operative.

Droplets

Vacuum arcs emit micron sized metal droplets (3) parallel to the cathode surface with velocities of the order of 10-100 m/s, due to the very high power density at the cathode spot. The droplet formation and ejection are linked to many mechanisms. These include a) local heating of the cathodic material and formation of a molten pool, b) transport of the liquid metal to the periphery of the molten region by accelerated ions and plasma pressure and c) droplet charging and extraction by strong electric fields and momentum exchange by ions.

A number of techniques (11) have been developed for reducing droplet contamination. Increasing cathode spot velocity by magnetic steering is the most successful of these. Another popular technique is to use a toroidal magnetic filter to guide the plasma. The droplets, which follow straight trajectories, are lost within the duct. The ducts are very inefficient in terms of mass transport; 25 % is considered good.

Instabilities and splitting of the plasma have been observed in some experiments.

Anodic Arcs

In anodic arcs, the metal vapour is generated by the evaporation of the anode. The cathode provides the electrons and can be carbon, metal or alloy. The electron emission can be thermionic with the cathode externally heated. Other possibilities include a hollow cathode configuration or a cathodic arc. The anode material can be in the form of a wire continuously fed into the discharge to compensate for the loss of length due to evaporation or the coating metal introduced into a crucible made of refractory material.

The basic physical mechanism underlying the anodic evaporation is the heating of the material due to electron bombardment Furthermore, the electrons also excite and ionise the evaporated atoms in front of the anode due to inelastic collisions. The anodic source produces a unique point source of pure metal vapour plasma. The coating is generally free of macroparticles since the vapour emission is from the ohmic heating and is free of violent processes like sputtering etc. The decoupling of the electron emission mechanism from the input arc power make the anodic arcs more flexible for applications of a large variety.

For arcs with currents upto 200 A, deposition rates upto 100 nanometer/sec have been obtained in laboratory scale trials. The degree of ionisation, which is the fraction of the ionised flux to the total flux, is of the order of 20 per cent for a variety of materials.

6. High Frequency Capacitive Discharges

We saw that the application of a dc voltage of few hundred volts to electrodes in a low-pressure gas leads to the production of glow discharge plasma. What happens if this dc power supply is replaced by a source of alternating voltage of high frequency?

Power Flow

The mechanism of power flow from the RF electric field to ignite the plasma has the following sequence of events: The free electrons between the electrodes follow the oscillation of the electric field with a lagging phase difference of 90°. This response is essentially inductive and means that there is no net absorption of energy since the work done on the electron averages to zero in time. The presence of electron-neutral collisions quantified by Ramsauer[1] cross sections (fig. 3.12a.) change the electron momentum adding a resistive component to the electron motion. This is also aided by the electron-electron collisions described by the Gvosdover[2] cross sections, which are larger than electron-neutral collision cross sections at electron energies less than 10 eV (fig.3.12b). RF power absorption and randomisation lead to electron heating. The electrons in the tail of the energy distribution acquires enough energy to ionise the neutrals leading to cumulative build up of electron-ion pairs and ignition of the plasma. The bulk plasma is separated from the electrodes through sheaths, which connects the plasma potential to the electrode potential. The sheaths with space charge have strong electric fields and are capacitive. The electrical equivalent of a capacitive RF discharge is shown in fig.3.14.

Electron Heating Mechanisms

In addition to this classical type of Ohmic heating of electrons, energetic electrons can be produced by the acceleration of secondary electrons produced by ion bombardment from the electrodes, as in the case of the dc glow discharge. However, RF plasma has another novel route for electron heating. In the RF plasma, the sheaths near the electrodes are time-dependent because of the oscillatory voltages on the electrodes. The successive contraction and expansion of the rf sheaths during the polarity change on the electrode gives rise to a stochastic heating. During sheath expansion, electrons at the sheath edge gain energy from the sheath electric field. The advancing sheath can be considered as an electrostatic wave and the electron as a particle riding this wave and gaining energy.

In the capacitively coupled system, the amount of rf current which can be driven into the plasma in order to maintain it is limited by the amount of current which can pass through the sheath. For the desired conditions, the sheath impedance dominates, the plasma density is proportional to the square root of the power for electropositive gases. Thus, the plasma efficiency decreases as the power increases and the sheath voltage increases.

The power transfer from the external circuit to the plasma takes place when the driving frequency is comparable to the momentum transfer collision frequency. This has led to the investigations of the diode reactor at higher driving frequencies. At these frequencies, the total impedance of the plasma is reduced resulting in reduction of the applied voltage across the diode. Both the real and imaginary parts of the impedance decrease at higher frequencies, with the decay of the latter more pronounced. The reduction of the imaginary part is interpreted as due to the reduction of the sheath thickness and hence the sheath capacitance. This is a good result since more of the driving power is dissipated in the bulk leading to the enhancement of the breeding. The reduced electrode voltage also results in reduced ion energies.

RF Power Coupling

Because of the high electron mobility in a plasma (rf or dc), a rf diode system tends to develop large electron currents during the positive portion of the applied rf cycle. Usually a large capacitor (500-2000 pF) is placed in series between the rf power supply and the powered electrode, or electrodes if the anode is not grounded. The large series capacitor allows a significant negative bias to develop on the cathode, typically half of the value of the applied peak-to-peak rf voltage. This bias is then the acceleration voltage for ions from the plasma, which move much too slowly to respond to the applied rf potentials.

Another major difference between RF and dc discharges is in the plasma response to the external power circuit. The external driving circuit, which usually has impedance of 50 ohm is not matched to the complex, reactive impedance of the plasma contributed by the capacitive and inductive components. An impedance matching tuning network provides the complex conjugate to match the power supply and plasma impedance.

In addition to the series capacitor, it is common to use two other tuning components to help match the impedance of the plasma to the output impedance of the rf power supply. These components, usually a shunt capacitor to ground and a series 3-4-turn inductor, are located along with the series capacitor in the "matchbox," which is physically located adjacent to the cathode position. The inductor is fixed, and both of the capacitors (shunt and series) are variable. A control circuit within the matchbox controller senses the reflected power (from the matchbox and plasma back to the power supply) and adjusts the variable capacitors to minimise the reflected power. Usually this is done automatically by means of reversible motor drives on the capacitors, but occasionally laboratory-based systems will have manual controls for the tuning network.

7. High Frequency Inductive Discharges

If an inductor coil is kept in the vicinity of a metallic surface, and energised by driving a high frequency current, a voltage of magnitude V = - d/dt (where is the magnetic flux in the coil) will be induced in the metal driving a current in the opposite direction. This is Lenz’s law, utilised in industrial induction heating applications. The layer in which current is driven is called the skin depth of the metal and is given by the expression:

$$\delta_s = \{1/\pi f \mu \sigma\}^{1/2}$$

where f is the frequency, the magnetic permeability of the material and the conductivity.

If a region of low-pressure gas as replaces the metal surface as shown in fig.3.15, and the voltage is adequate to break down the gas by the process of electron avalanche as in the case of dc electric fields, we can form an inductive discharge plasma. Hittorf discovered this in 1884. In the inductive plasma, the RF coil acts as the primary and the plasma acts as the secondary of two coupled coils.

For frequencies below the plasma frequency ${}_p$, and assuming that electron-neutral collisions are rare, the plasma is a good conductor and has a skin depth given by $c/{}_p$ where c is the velocity of light.

In the absence of collisions between electrons and neutrals there would normally be no net power absorption. However, ICP devices exhibit an anomalous heating effect. From classical electromagnetic theory the rf inductive field must decay in a skin depth $d = c/{}_p$. In a collisionless situation, electrons can be accelerated and decelerated by RF fields within the sheath acquiring no net energy. However, if the electrons have a thermal velocity and if they can traverse the skin region in a time short compared to the RF period, that is:

$$d < v_e$$

they will gain net energy from the rf field. An immediate consequence of this is that the field at one point can affect currents in other parts of the plasma (17). The other effect is that the collision frequency is modified because the transiting electron can carry momentum away from the field. Turner has calculated this anomalous skin depth as

$d = (c^2 v_e / /_p{}^{2})^{1/3}$

The non-local effect of RF current diffusion is that the current induced by the field at one point can be transferred to another point by thermal electrons and produce additional electric field interfering with the local field. The field and current become independent of each other to some extent. The RF current can be of opposite phase to the local field resulting in a local negative energy transfer from the electrons to the field. The axial distribution of electric field and current in an experiment by Godyak and Kolobov (18) are shown in fig.12. The non-monotonic distribution shown is typical for the anomalous skin effect. The positive and negative RF power absorption is localised to certain regions.

8. Electron Cyclotron Resonance Discharges

We saw earlier that an electron moving with a velocity v in a magnetic field of magnitude B experiences a force of magnitude evB in a direction perpendicular to both the velocity and the magnetic field. The result is that the electron orbit is constrained to becomes a circle and the frequency of the circular motion given by f = eB/2m which is called the cyclotron frequency. If an oscillator electric field with an electric field vector parallel to the direction of electron motion and frequency equal to the cyclotron frequency is imposed in the region of the gyrating electrons, the electrons would effectively see a steady electric field and hence can be accelerated by it. Electron cyclotron resonance or ECR discharges are based on the phenomenon of this resonant interaction between electric and magnetic field. The circular electric field can be imposed by electromagnetic waves.

High power microwave sources are available at the frequency of 2.45 GHz and hence commercial ECR plasma sources have been built around these sources. The magnetic field required for cyclotron resonance is 875 Gauss. The basic magnetic field configuration is shown in figure 3.16. Microwave power is injected into the region where air core coils generate an axially uniform or diverging solenoidal magnetic field.

The second and more popular version uses multipolar field generated by permanent magnets like SmCo. In the DECR device, a set of cylindrical conductors each located a few millimetres above the pole face acts as the microwave applicator. Upscaling is simple, though the conductor location within the plasma region tends to generate impurities. A recent innovative solution of this problem has resulted in the SLAN sources, where a slotted antenna located between pole faces inject microwave power from a ring cavity (see fig x).

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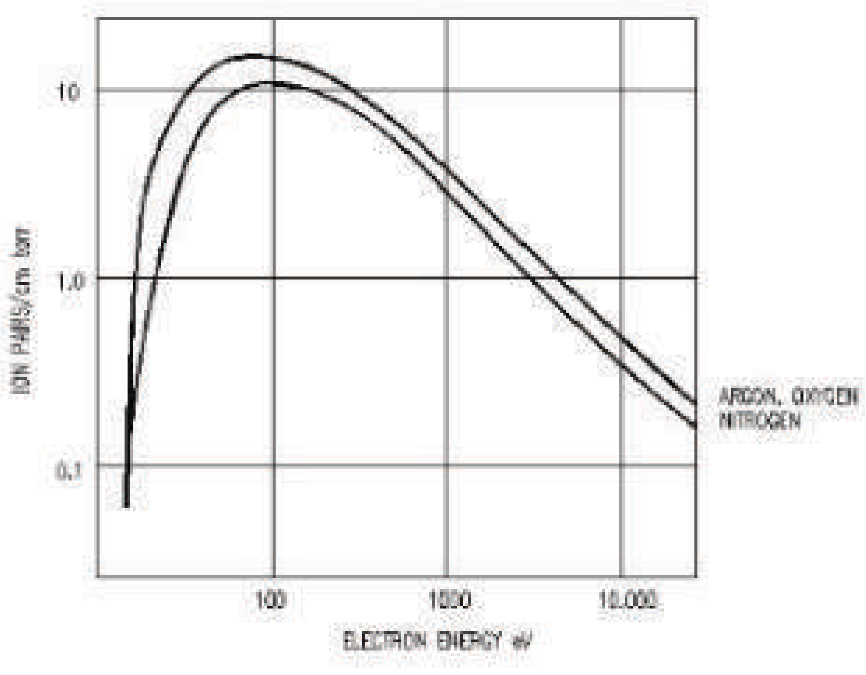

Fig. 3.1. The cross section for electron impact ionisation has a maximum at energy between three and six times the ionisation

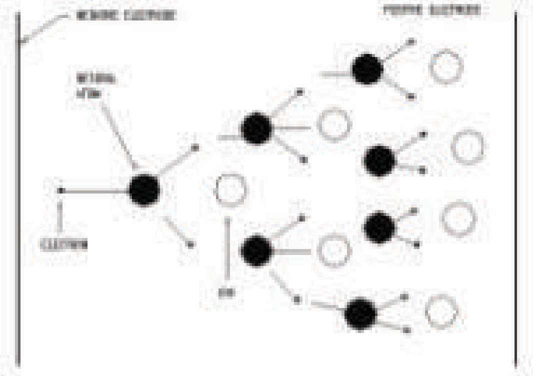

Fig. 3.2. Schematic diagram showing the avalanche mechanism of electrical breakdown.

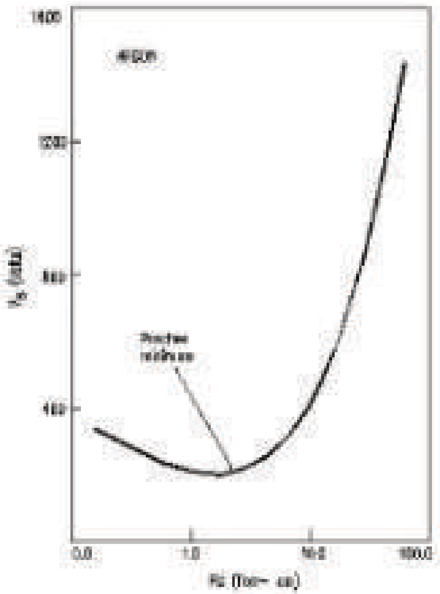

Fig. 3.3. The relationship between the voltage for breakdown of the gas to the pressure and the electrode separation is given by the Paschen curve

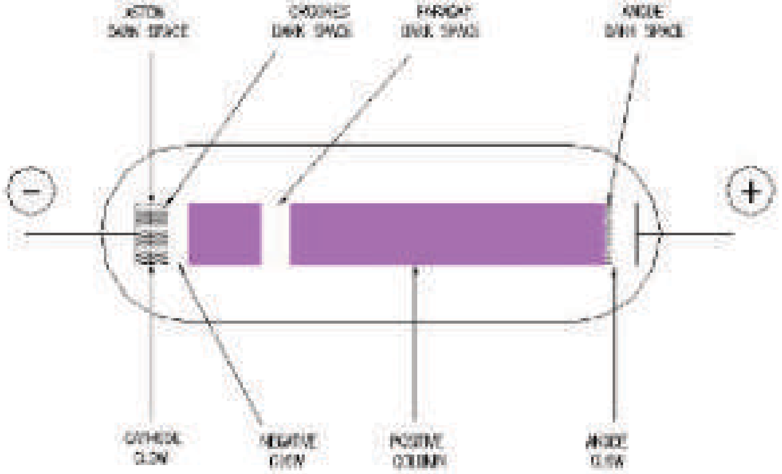

Fig. 3.5. The generic features of a glow discharge showing various regions of luminosity

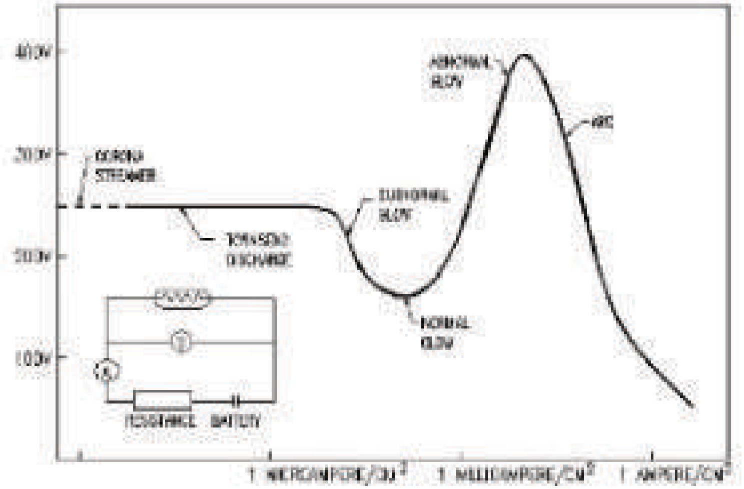

Fig.3.4. The general behaviour of a dc electrical discharge can be represented in terms of their voltage current relationship

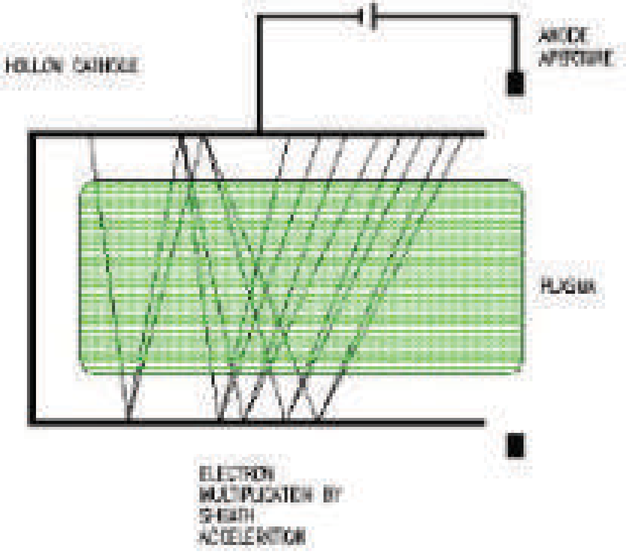

Fig. 3.6. The hollow cathode discharge increases the efficiency of ionising electrons by trapping them in the cathode sheath

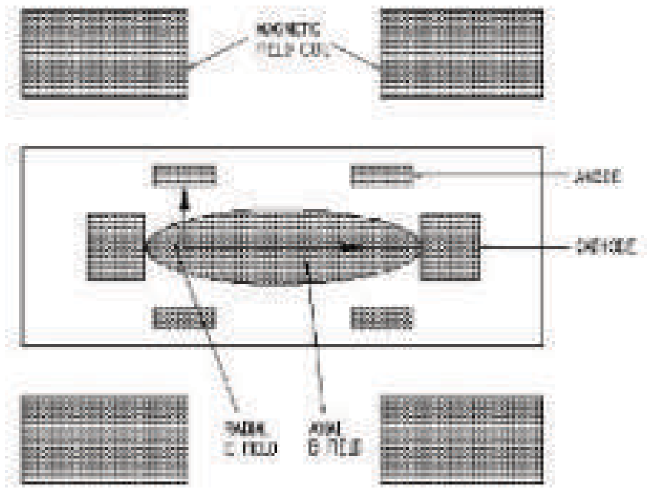

Fig. 3.7. In the Penning discharge, electrons are trapped between the two cathodes by an axial magnetic field

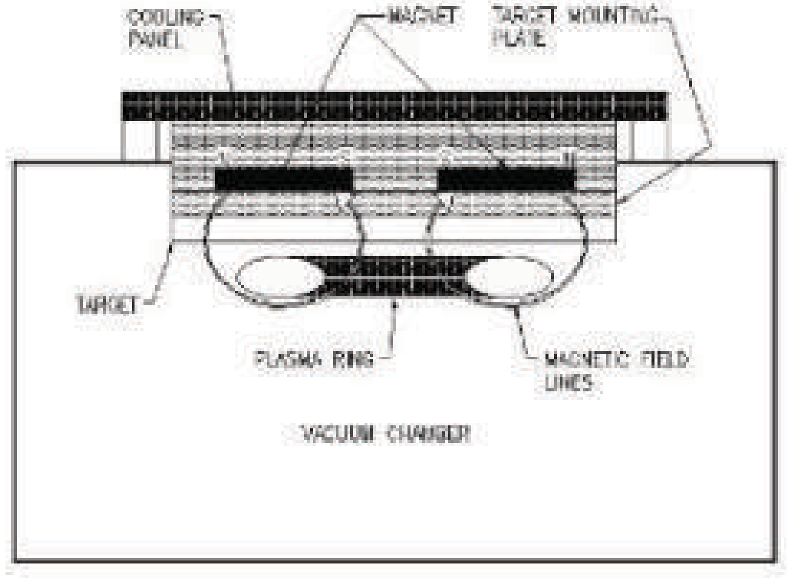

Fig. 3.8. The electron confinement in a magnetron is due to the presence of orthogonal E and B fields at the cathode surface. This results in an E x B drift for electrons (the Hall effect)

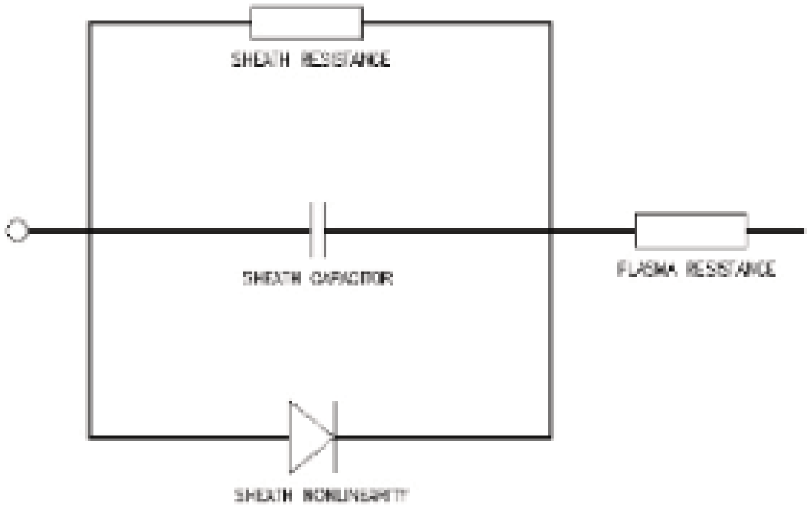

Fig.3.9. The electrical equivalent of a capacitive RF discharge

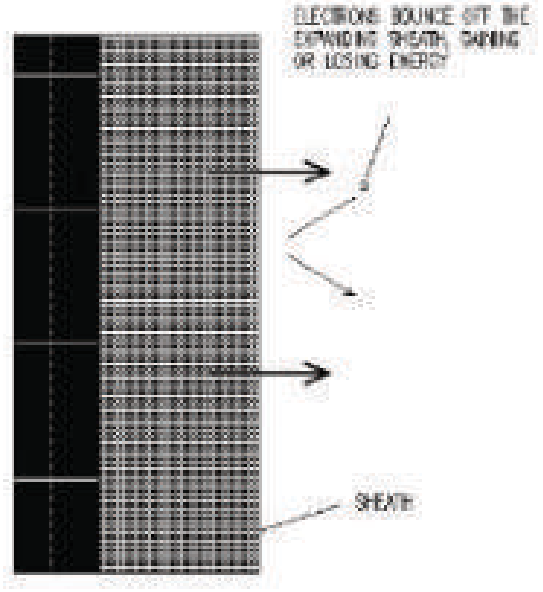

Fig. 3.10. Electrons can be stochastically heated due to sheath movement

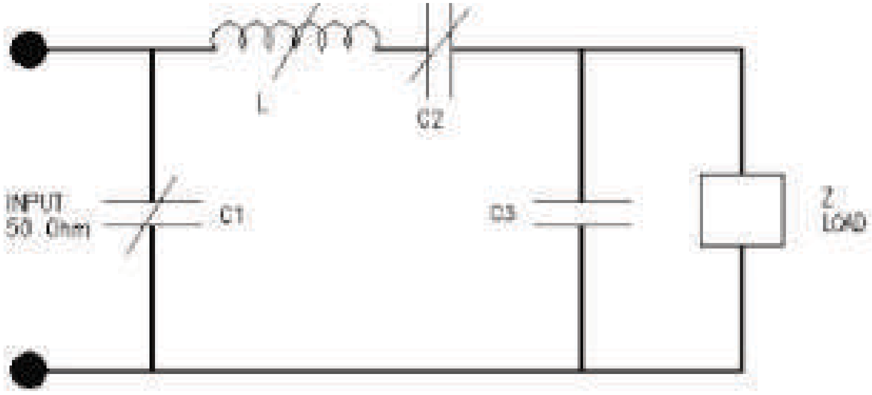

Fig. 3.11. Method of matching the impedances of RF source and plasma

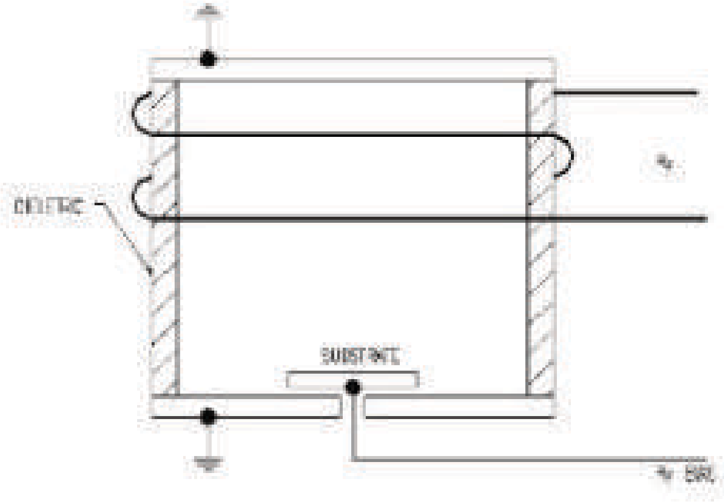

Fig. 3.12. Concept of the inductive discharge, which produces electric field for gas breakdown by time varying magnetic flux

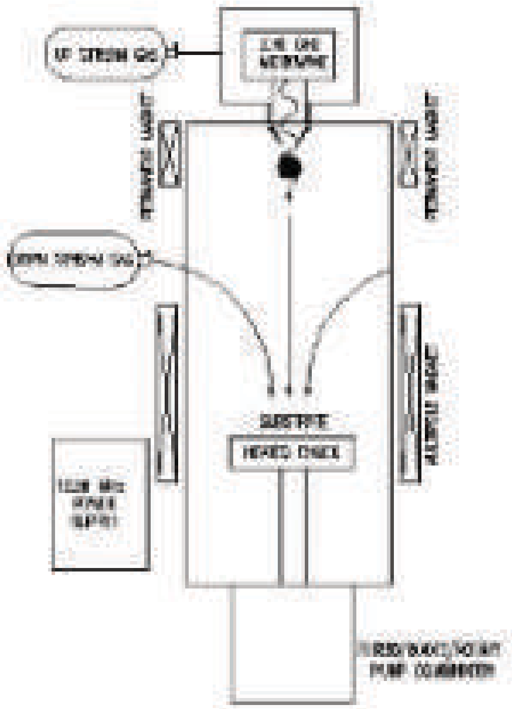

Fig. 3.13. The ECR plasma source utilises the resonant energy transfer from a high frequency electric field to the electrons gyrating around the magnetic field lines

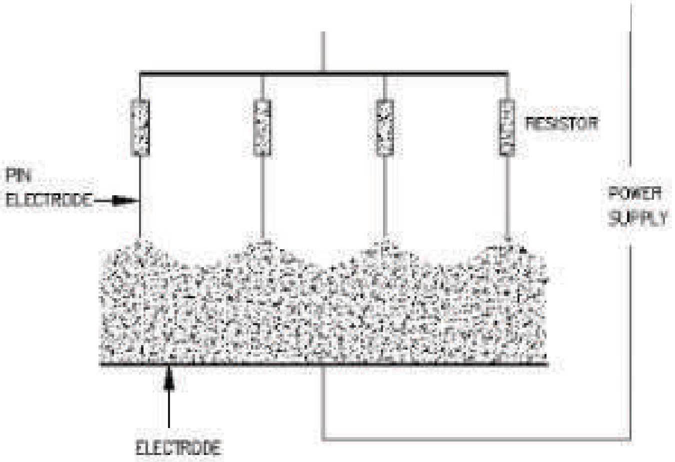

Fig. 3.14. Methods of producing atmospheric pressure glow discharge (a) using sharp electrodes (b) using micro hollow cathodes (c) using a primary discharge as the source of electrons for a secondary discharge

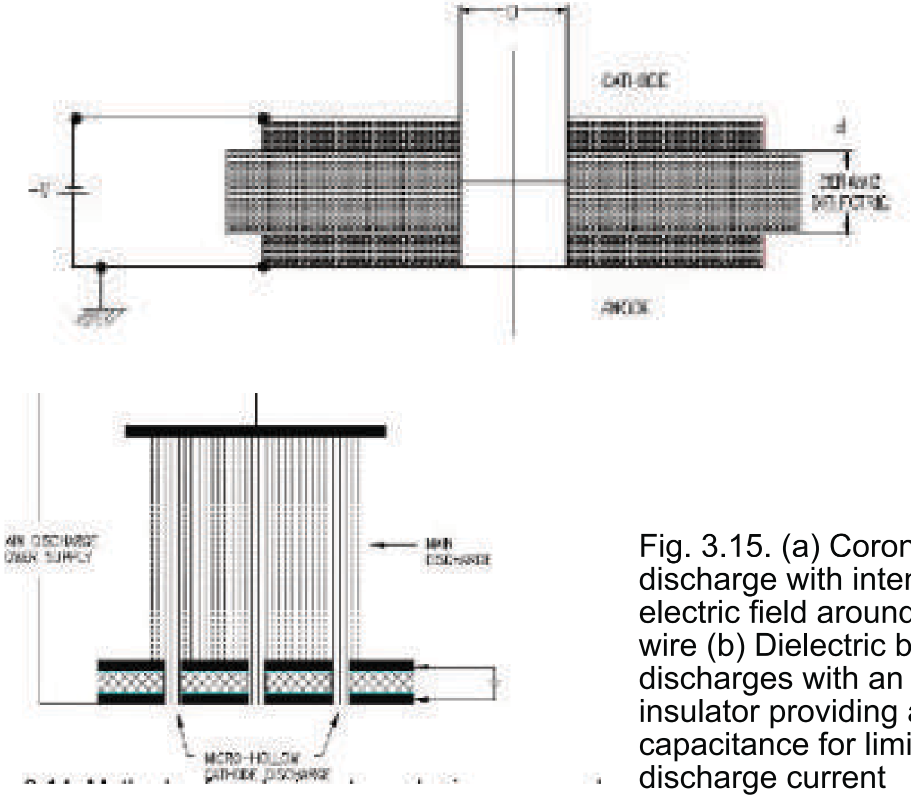

Fig. 3.15. (a) Corona discharge with intensified electric field around a thin wire (b) Dielectric barrier discharges with an insulator providing a capacitance for limiting discharge current

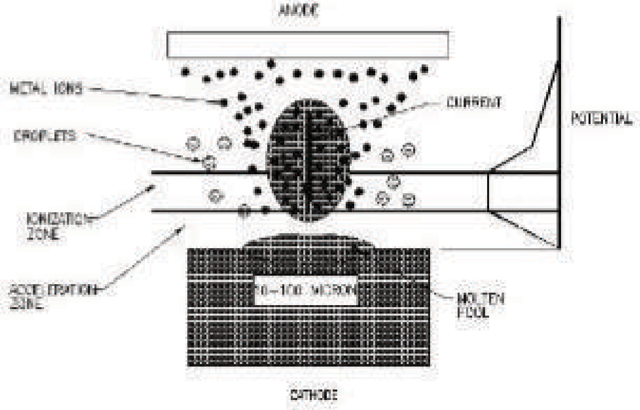

Fig. 3.16. Vacuum arc phenomenology showing the emission of metal vapour and droplets. The potential distribution in the cathode anode space is also shown

4. Plasma as an Industrial Tool

Material Processing with Plasma

Interaction of plasma with solids and gases is the basis of plasma enabled material processing. The four foundations of plasma processing are the ability to produce energetic particles, sputtering process to generate metal atoms, chemical reactivity and the efficient conversion of electricity to heat. These, individually or in tandem can produce a number of effects, which have industrial applicability. This chapter discusses these aspects in some detail.

The Processing Plasma

The unique properties of the Plasma State make it a powerful industrial tool. These are based on the following effects, characterising the plasma environment:

1. Presence of electrons, which can extract energy from electric fields.
2. Conversion of electron kinetic energy into space charge electric fields and thermal energy.
3. Tendency of the plasma to shield and localise externally applied electric potentials creating intense electric field regions called sheaths or double layers through which plasma particles can be accelerated.
4. Creation of chemically active species from neutrals by collision with energetic electrons and ions.
5. The interaction of energetic plasma particles with surfaces to release particles by sputtering and evaporation.
6. The background of energetic radiation in plasma produced either by atomic processes or by interaction with electromagnetic fields.

Quite often, many of these effects manifest simultaneously in a plasma reactor. While this results in a wealth of phenomena, it also leads to an obscuring of the cause-effect relationship. This has hindered the development of plasma processing into a precise science. Plasma processing is one of the disciplines where application has led science. But this situation is changing because of the realisation that understanding the science behind a process is crucial to its improvement.

Certain plasma properties can be optimised and enhanced leading to a focus on a particular application. Thus we have fusion plasmas where particle temperatures are enhanced, impurity content minimised, and confinement enhanced or MHD plasmas where flow velocity and conductivity enhanced. In the same spirit we can define processing plasmas where the parameters relevant to plasma processes are enhanced or optimised.

The physical processes of interest in processing plasma are the following:

1. Conversion of electrical energy into ionisation and heating of the feedstock gas
2. The formation of species of required chemical reactivity or other properties
3. Transport of energy, momentum and mass to the process region or boundaries including transport to the electrodes
4. Quenching or termination of the reaction at appropriate time and the removal of the product

The process plasma, thus defined, differs from other plasmas in a number of ways. First of all, there is no confinement required and in fact one prefers de--confinement since the throughput of processing depends upon fluxes of ions and electrons depositing their energy on the process substrate. Hence, there is often a lack of equilibration between species. This means that the characteristics of plasma formation and loss will imprint certain properties on the plasma. Secondly, we will see that the species, which are used to form the plasma, determine some of the properties due to the specific atomic physics and chemistry. In the context of plasma processing, Oxygen and Nitrogen plasmas are as different as plasma and neutral gas.

An ideal plasma-processing reactor with the associated processes and inputs can be schematically represented as in Fig 4.1. Plasma generation, gas phase chemistry and surface and material interaction processes primarily determine the functioning of the reactor. Each of these requires inputs from plasma and material sciences, which determine the spatial and temporal variation of relevant quantities. The operating and design parameters are made up of a combination of initial and boundary conditions and input data such as gas composition, pressure, flow rates, power etc. Another set of input data involves species interactions with each other and boundaries such as cross sections, rate and transport coefficients, and emission, reflection and sticking coefficients etc. The processes themselves vary in space and time for plasmas are notorious for involving disparate time and space scale lengths.

Plasma generation encompasses ionisation reactions, charged species transport and kinetics and electromagnetic theory. The plasma generation and gas phase phenomena are coupled through collisions between electrons, ions and neutral species. The reacting species are created by the collisional processes experienced by the constituent particles of the plasma. Plasma-material interaction and its evolution during processing is perhaps the most important because a modified surface or a surface synthesised by plasma is the product of plasma processing.

Each plasma process operates in a restricted multi-dimensional parameter space and the volume of this space determines the overall economics, quality, performance and other parameters, which will make the process competitive and industrially relevant. There are a number of constraints imposed on this operating window. There can be process limits imposed by the plasma and reaction rates, efficiency limits imposed by how electrical energy is converted into plasma density, emission limits imposed by what fraction of the process raw materials are consumed in the process etc.

Plasma assisted manufacturing use plasmas in the following ways:

1. Plasma as a source of heat
2. Plasma as a chemical catalyst
3. Plasma as a source of energetic ion and electron flux
4. Plasma as a source of sputtered particles

These are schematically represented in fig. 4.2.

These fundamental properties manifest themselves in a variety of basic processes, which form the basis of plasma based manufacturing [Fig. 4.3]. Each of the fundamental process, either individually or in combination, leads us to a variety of applications. For new chemicals can be produced in plasmas by plasma chemical synthesis. A film can be deposited by polymerising such particles on a surface. In the following sections we shall examine these in some detail.

Plasma as Source of Heat: The Plasma Torch

There is no theoretical limit to the temperature that can be obtained in a plasma jet. Combustion flames give a maximum temperature of about 4000 degrees and the maximum heat flux for an oxy-acetylene flame is about 0.3-kW/ cm^2. Generation of heat in the arc plasma is through the ohmic dissipation of electrical energy in the discharge column and is relatively independent of the species involved. Typical atmospheric pressure arc plasmas have a temperature field ranging from a few thousands to tens of thousands of degrees. This results in access to high temperatures in both combustible and non-combustible materials.

The workhorse of thermal plasma processing is the plasma torch or plasmotron. Plasma torches produce plasmas by sending electrical currents at high voltages through an initially nonconducting high-speed gas flow with the plasma being extracted as a jet through an opening in the electrode and out of the confines of the cathode-anode space. Plasma temperatures can easily reach tens of thousands of degrees and high enthalpy gas flows capable of creating large reaction volumes can be generated. The inherent thermal and electromagnetic instabilities of the arc column are stabilised by forced gas flow (sometimes vortex) along the current path or by interaction with a guiding wall or by external magnetic fields. Arc, RF and microwave plasma sources can be converted to plasma torches.

The driver for the development of plasma torches was the space race in the 1960's, which saw rapid advances in missile technology. Missiles re-entering the atmospheric air create shock-ionised plasma. This condition had to be simulated in the laboratory for the development of materials capable of withstanding the searing heat of the re-entry plasma. Simulation arc systems were primarily designed to generate the re-entry conditions using clean, high enthalpy gases at high stagnation pressures. Many of the present day plasma torches are derivatives of the plasma jet sources built for this application [Gage 1959].

The two basic configurations of plasma torches are given in Fig.4.4. The arc is generated at the conical cathode tip usually made of Tungsten doped with Thorium. The plasma generating gas is injected through the tip, thereby cooling it and enters the plasma at the constriction point. A variety of materials such as Stainless Steel, Copper alloys and most of refractory metals can be used as cathodes. The anode can be the work piece itself as in Fig.4.4a or an independent electrode as shown in Fig. 4.4b. The former is called a transferred plasma torch and the latter a non-transferred torch. The cathodes can also be of the hollow geometry [Fig.4.5]. A magnetic field is sometimes used to continuously move the arc root over the cathode surface.

The performance of most plasma generators using electric arcs is determined by the design of the electrodes. The cathode is the critical component of an arc plasma torch [Gauvin 1989]. While the cathode design is the dominant factor in determining the limitations in torch life, operating current and power level, the anode design dominates the functional performance for most torches, i.e. the heat and momentum transfer to the materials to be processed.

The four basic geometries of the cathodes are tubular, ring, rod and button. The tube and ring geometries are generally made from electrode grade Copper and are water-cooled. The rod and button geometries are usually made Thoriated Tungsten or refractory metals embedded in a water-cooled Copper holder. Graphite, a popular choice, can be operated without cooling. The temperatures in the arc attachment zones are much higher for Tungsten electrodes than for Copper electrodes. Field emission dominates in copper electrodes whereas thermionic emission dominates the tungsten and graphite electrodes.

Cathode of the plasma torch can be thermionic or cold. Thermionic cathodes consist of a refractory material in form of a rod or button. Doping with a low work function material enhances electron emission. Electron emission being the dominant cooling mechanism, the arc current density and the electron emission characteristics of the cathode material determine its spot temperature. Low work function dopants, are preferentially lost by evaporation. This, however calls for a careful consideration of materials balance for optimal cathode design. The loss channels include material transport by diffusion in the refractory metal matrix, evaporation and redeposition in form of ion flux or in form of regular vapour deposition in the cooler regions of the cathode. The cathode spot will be molten at high current densities, and hence dissolution of plasma gas atoms in the cathode material and ejection of molten metal droplets from the cathode have to be additionally considered. In thermionic cathode design, there is also a need to consider the arc diameter in relation to the diameter of the emitting spot. For example, too strong cooling of the cathode by conduction may reduce the size of the emitting spot, leading to higher electric fields in the sheath region, increasin the chances of erosion. Plasma torches with thermionic cathodes operate at power levels ranging 100 W to several megawatts. Arc currents range from a few amperes to thousands of amperes.

Cold cathodes consist of a water-cooled metal. Here electrons are supplied to the arc by evaporation and ionisation of the metal in a very small cathode spot. Consequently, electron emission and material loss are integrally connected. In comparison with thermionic cathode attachments, the cold cathode attachment is unsteady, since it depends not only on the cathode material and the arcing gas, but also on the physical and chemical surface conditions, which undergoes a change during the arcing process. Forced movement of the cathode attachment by means of magnetic fields and/or transverse fluid flow are sometimes employed to minimise cathode erosion. This motion can be enhanced by the addition of impurities to the plasma gas, which apparently result in changes of the surface condition, which then increase the arc attachment velocity. Cold cathode torches are available for power levels from about 100 kW to 10 MW, and for currents from 100 A to a few kilo amperes.

Moreover, the presence of oxygen in the plasma generating gas causes very high erosion rate of electrodes, especially due to production of fragile oxides on the electrode surface. Special electrode materials and configurations are used in torches with air or water vapour. A consumable Graphite cathode can be used, or for lower currents Hafnium and Zirconium cathodes have been tested.

Anodes are water-cooled electrodes located outside the arc chamber, downstream of the exit nozzle. Thus, the plasma jet between nozzle exit and point of anode attachment is heated by passage of electric current. This arrangement leads to some special characteristics of plasma jet, which originate in Joule heating of the jet as well as in interaction of secondary anode jet with the main jet. Arc axis and flow can be perpendicular to or parallel to the anode surface. The anode configuration with the anode surface perpendicular to the arc axis and the plasma flow directed towards the anode is a typical arrangement in transferred arc reactors. The workpiece itself acting as the anode is the most popular in melting configuration. All possible combinations are encountered in commercially available torches.

Several factors contribute to the heat flux [Pfender 1993]. In general, condensation of the electron on the anode material and the transfer of the electron enthalpy are the most important ones. Typically 50 per cent of the anode heat flux is due to current flow, approximately 45 per cent by conduction/convection and the reminder by radiation, although distribution is a strong function of the arc configuration and parameters [Sanders 1984]. Total anode heat flux in steady arcs may be in the range of 1-20 kW/cm^2 and it may reach values of the order of MW/ cm^2 for pulsed arcs. The very high energy flux as a result of high temperatures, high gas flow velocities and high thermal conductivity of plasmas permit high reaction volumes.

For a typical stagnation flow conditions, the plasma flares out to attach to the anode surface. The steep gradient in electron density between the anode surface and the plasma leads to an electron diffusion flux, which conducts the current. Diffuse attachment results in a negative anode fall. At reduced flow towards the anode, the arc constricts and the arc temperature is enhanced in front of the anode. This constriction leads to the formation of an anode jet directed towards the incoming plasma flow and a stagnation point some distance away from the anode surface. The heat flux distribution in this mode of attachment is more strongly peaked than in the case of the diffuse attachment, although the total heat transfer may be the same.

When the plasma flow is parallel to the anode surface the current path has to cross a cold gas boundary layer between the anode surface and the arc column. This is generally unsteady. The competition between the drag caused by the flow in the cold boundary layer on the highly viscous plasma channel between the arc column and the anode surface and the Lorentz force due to the self-magnetic field and the curvature of the current path determine the motion of the anode attachment. The relative magnitude of these forces is in turn determined by the thickness of the cold gas boundary layer. For a thick boundary layer, the arc anode attachment slides downstream until the potential gradient across the boundary layer at an upstream location becomes sufficiently large for a breakdown resulting in a periodic variation of the arc length. This is termed the restrike. Increase of the arc diameter due to a change in arcing gas for the same arc current and the same anode diameter will reduce the boundary layer thickness and facilitate a breakdown across the boundary layer. This ‘takeover mode’ results in a random variation of the arc length. Increasing the arc current for the same channel diameter and the same plasma gas flow rate will also result in a decrease in the boundary layer thickness and a simultaneous increase in the magnetic forces driving the arc attachment upstream, again resulting in the operating mode. While the movement of the anode attachment has the advantage of reducing anode erosion, the resulting variation in arc voltage and power will produce variations in the enthalpy levels in the plasma jet and, therefore, in the heating rates, and result in fluid dynamic instabilities of the jet. On the other hand, operation in the stationary attachment mode will result in high anode erosion rates, lower power levels and, because of the short arc, in lower torch efficiencies. Quantitative description of these phenomena requires a three dimensional dynamic model which is not yet available.

Heat transfer to particles immersed in the plasma has attracted considerable attention because of its relevance to applications such as plasma spraying and in-flight processing [Pfender 1989]. In spite of this there are large discrepancies in the quantitative evaluation of heat transfer co-efficient. Drag, convective heating and cooling affect the rates of heat, momentum and mass transfer between plasma and the particles. The boundary layer surrounding the particle is characterised strong deviations from chemical and kinetic equilibrium. Other affects such as vaporisation and evaporation of particles can also contribute to heat transfer [Pfender 1993]

The performance of a torch will depend upon how efficiently electrical energy is transformed into thermal and radiation energy in the arc column. The electrical conductivity of the plasma formed from various gases play an important role in determining this efficiency. The electrical conductivity of commonly used plasma gases (Ar, N_2, H_2) is roughly similar (about 2000 ohm-m^{-1}) at 10,000^o K.

Two variables are available for manipulation when operating a plasma torch; arc current and gas flow rate. Also important in this respect is the total enthalpy of the plasma gas, which is the sum of the heat capacity $C_p dT$ and of the heat of dissociation and ionisation. The radiated energy is a function of the temperature, volume of gas and emissivity coefficients. The temperature gradients are also an important characteristic of arc plasmas since for most applications the input power and enthalpy are the most preferred indicators of the torch performance. Figure 4.6 shows the relationship between input power and enthalpy for a ScanArc plasma torch. Fig. 4.7 relates the thermal efficiency with enthalpy for the same torch.

In many applications, a material cathode with the inevitable material erosion and contamination may not be acceptable. The electrode-less RF inductive plasma torches were developed for such situations [Fig. 4.8]. The design can be traced to Reed in 1961 [Reed 1961]. The basic scheme is not very different from the inductive plasma source described earlier. The cold gas injected into the plasma extracts energy, gets heated up and ejected as a plasma jet. The flow is tangential, which creates a vortex with low pressure near the axis. This serves to draw the plasma away from the walls. However induction plasma torches have not found wide spread application because of the poor efficiency of coupling RF power into the plasma. Typical efficiencies are in the range of 40-50 per cent and can drop significantly at high power rating [Fauchais 1997]. Higher frequency microwave power is also emerging as an energy source for plasma torch application [Woskov 1996]. The advantage of this approach is that 2.45 GHz microwave power generator from commercially available magnetron sources is much cheaper (typically $1/watt) than RF power. Both RF and microwave plasma torches produce plasma jets with temperatures lower than those, which can be obtained from electrode torches.

Thermal plasma sources provide unique advantages in material processing applications [Jones]. Plasma systems allow independent control of the chemistry due to the choice of the reactivity environment. Oxidising, reducing or inert environment can be created at will. Energy supplied to the system is independent of the Oxygen potential, making the plasma flame more versatile than a combustion flame. Reduction of oxides like Chromium, Magnesium, Manganese, Silicon, Titanium, and Aluminium, which are endothermic or require strongly reducing conditions are appropriate for plasma furnaces. The feed rate and power can be controlled independently and the electrical conductivity of materials does not limit the input power. This allows greater freedom of choice with regards to charge composition, without having to consider its electrical characteristics.

Moreover, the direct use of fine materials is possible, without the need for costly agglomeration. Plasma systems can operate with a wide range of gas flow rates allowing fine particles to be introduced in a flowing stream reactor.

Plasmas can be manipulated by magnetic and gas velocity fields to produce controlled physical configurations and can be used as a medium for in-flight processing free of material boundaries.

Non-equilibrium nature of the plasma implies very large temperature differentials between the plasma and the wall within sheath dimensions of millimetres. Thus quenching rates of a few million degrees per cm is commonplace in plasma reactors.

Computer modelling plays an increasingly vital role in the design of plasma torches. Arc modelling generally consists of solving the conservation equations of mass, energy, momentum and current, for the arc column and also for the arc electrodes. These four equations determine the principal arc quantities such as temperature, pressure, plasma velocity and electric potential for any given arc current. The material functions of the plasma, the electrodes and also, for arc welding, the molten electrodes, namely thermal and electrical conductivity, viscosity, density and specific heat, need to be incorporated as a function of temperature. With the availability of modern high speed computers, and the careful use of recently developed numerical methods, this level of detailed computation is quite feasible. Approximations need to be made for treatment of the electrode sheath regions. However for currents of 100A or more, detailed treatment of these regions can be omitted.

Plasma as a Chemical Catalyst

Molecules can react chemically only when they have enough energy to overcome the activation barriers. In conventional chemistry this energy is transferred to molecules by collision with other molecules or the wall. Vibrational energy is transferred in a stepwise manner until the lowest reactive state is reached. On the other hand, electron collisions with molecules can transfer much larger energy in a plasma environment, transforming the neutral molecules to a variety of excited species or dissociating them. New species like super-excited neutrals, positive and negative ions can be formed. Plasma becomes a powerful chemical tool and takes the role of a catalyst, as these new species cannot be generated in conventional chemistry in significant quantities. The lowering of the reaction temperature or the increase of a reaction rate at a given temperature are widely recognised effects of the plasma

However, excitation and dissociation by plasma electrons with broad energy distribution are not selective. The large variety of reactive species present in a plasma system lead to a large number of reactions and it is almost impossible to control the decisive ones of specific importance.

The comparison of energies of species in non-equilibrium plasma with the typical energy of chemical bonds is given in table I. The energetic species can break the covalent bonds of molecules exposed to such environments. Novel chemistry is possible with the intervention of high-energy electrons in the tail of the electron energy distribution function and the strong microscopic electric field present in non-equilibrium plasmas.

The plasma environment facilitates many chemical reactions simultaneously. Dominance of a specific reaction depends on the process parameters such as type of gas, flow rate, pressure, applied power etc. Reactions are heterogeneous in the presence of boundaries and substrates. Competition between ablation and deposition governs surface-related processes. When organic vapours are used plasma polymerisation and deposition occur. During etching and deposition the material interacts with the gas phase active species and precursors through the surface. This means that the surface conditions such as contamination, the presence of inhibitors, barrier layers, the adsorption of gases etc. are important and affects the process kinetics and properties of the deposited films.

Highly reactive atomic species are produced by dissociating molecular species in plasma. The atomic species can, in turn, react with organic compounds [Suhr 1983]. Hydrogen atoms either add to double bonds or abstract atoms from other molecules. In oxygen plasma, ionisation and dissociation can form various products like O_2^+, O^+, O^- and O. In addition metastable states like O_2 (1 g) are formed. The main reaction of atomic oxygen is the addition of double bonds and conversion of CH bonds to hydroxyl or carbonyl groups. Nitrogen atoms react with both saturated and unsaturated molecules.

An interesting aspect of plasma chemistry is the synthesis of complex molecules from simple starting materials. Typical reactions that occur are: isomerization, elimination of atoms or small groups, dimerization/ polymerisation and destruction of starting material. For example, a mixture of methane, water, nitrogen and oxygen etc. under glow discharge eventually yield amino acids, which are the starting materials for life. Processes like cis-trans isomerization, cyclization and ring opening takes place in plasma. In addition to monomolecular processes, bimolecular reactions are also possible.

Plasma etching is a two-step process in which chemically reactive species are generated inside the plasma, which interacts with solid material to form volatile compounds which diffuse from the surface and are evacuated. An example is the dissociation of CF_4 releasing fluorine, which silicon to form SiF_4 gas. The result is microscopic milling of the surface [Coburn 1979]. Plasma etching is a generic terms which includes process varieties like reactive ion etching, reactive sputter etching and plasma ashing.

The type of surface modification will depend on the substrate and process parameters. The depth of treatment depends on substrate temperature, process time and diffusion characteristics of material. Plasma action is limited to surface etching for depth upto a few microns only. As a result the surface property changes but the bulk properties are preserved. The technique is used for making the surfaces cleaner, harder, rougher, wettable and adherent. The method is also used for thinning the samples to be studied by electron microscopy and for processing of semiconductors to fabricate ICs. Inert ion sputtering is more of a physical process than a chemically reactive plasma sputtering. In chemical sputtering reactions occur and volatile products are formed. The gases used are Ar, He, O_2, H_2, H_2O, CO_2, Cl_2, F_2 and organic vapours.

Plasma etching of silicon using fluorine is a technique widely used in semiconductor device fabrication. The three reactive steps are the following:

Chemisorption $[F_2 \quad F_{2(ads)} – 2F_{(ads)}]$

Reaction $[\,Si + 4F_{(ads)} \quad SiF_{4(ads)}]$

Desorption $[\,SiF_{4(ads)} \quad SiF_{4(gas)}]$

The chemical vapour deposition (CVD) is a high temperature reaction involving volatile metal donor precursors, which chemically decompose due to thermal energy. Chemical reactions relevant to CVD include pyrolysis, oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reaction, disproportionation, and chemical transport. The heated substrate acts as a catalyst, promoting dissociation. CVD processes are chosen to be heterogeneous reactions and the product is usually in the form of thin films (TiN, TiC) deposited on the surface. Materials deposited at low temperatures (less than 600o C) are amorphous, whereas higher temperatures promote polycrystalline films. The orientation of the crystals is determined by the substrate crystal orientation, a property known as epitaxy. CVD films have good stoichiometry, high density, excellent adhesion etc. However, the high deposition temperature (700-1500 C) makes the process limited to material, which can bear such extreme temperatures.

In plasma CVD, the reactivity of the plasma species generates the products that subsequently react and deposit on substrate surfaces [Veprek 1989]. A significant process improvement over conventional CVD is the lowering of the processing temperature. In addition, the ion bombardment can be used to modify film characteristics. Deposition takes place in four major steps:

1. Electron-impact reactions between electron and reactant gases to form ions and radical reactive species
2. Transport of the reactive products from the plasma to the substrate surface concurrently with the occurrence of many elastic and inelastic collisions in both the plasma and sheath regions
3. Absorption of the reactive species on the substrate surface, usually followed by reaction between the species and the surface
4. The reactive species and reaction products incorporate themselves on the substrate forming films or re-emit from surface back to the gas phase.

This technique is well established and is used to deposit thin organic and inorganic films (e.g. SiO_x, TiN, TiCN, diamond coating etc.) on metals, glass, polymers and on various other materials to protect their surface from corrosion and/or to improve surface hardness and wear resistance property.

Polymerisation is the creation of very large molecules by the joining of many small linkable molecules called monomers. Classical polymers have reactive structures such as double bonds that allow them to bond to one another; for example the double bond in methyl methacrylate provides the linking site for forming the plastic polymethyl methacrylate. This process can happen in the plasma as well. However, plasma can also polymerise materials, which do not normally form polymers under normal chemical route by fractionating gases that lack linkable sites into many new and reactive compounds that subsequently may polymerise.

The term plasma polymerisation [Millard 1974]. is traditionally used to mean processes occurring in surface film formation. Fragments of the decomposed and excited monomer form new molecules in the gas phase or on the surface. Deposition starts with sorption and proceeds in a stepwise manner. The adsorbed molecules subsequently interact and engage in ionic or radical polymerisation on the surface and thus form a thin film. Deposition is a result of the interaction of the active species both with each other and with the substrate surface. While the film is forming, the newly created surface atoms and molecules are subjected to the bombardment by the species from the gas phase and excitation by ultraviolet radiation from the plasma. Films thus formed are highly cross-linked, pinhole-free, chemically inert and adhere well with the surface. This process is schematically given in fig. 4.9.

A wide variety of organic compounds can be polymerised. Monomers such as saturated alkanes and aromatics, which are normally inert in conventional polymerisation, can be readily polymerised in the plasma environment. In the deposition of aliphatic and aromatic polymer films in plasma, all saturated or unsaturated monomers can be polymerised, including those that are resistant to polymerisation by the conventional techniques. Within a plasma polymerisation process, the initial monomer gas undergoes considerable chemical changes. Due to the physical and chemical complexity of the process and its strong relationship to process parameters, the film properties can be controlled during deposition and combine different features such as good adhesion of the film at the substrate surface and high hardness at the upper film surface. Plasma polymerisation can also produce structures which have a spatial gradient in their physical properties, e.g. of the refractive index versus film thickness.

Plasma as a Source of Energetic Particles

A directed stream of energetic particles has been proven to be a versatile tool in many material processing applications. Ion-beam milling is a process of atomic scale removal of material from surfaces and is used in etching of surfaces with precision and directivity. Extremely high precision and control possible at the micrometer and nanometre dimensions have rendered processes like plasma chemical etching, film deposition etc the mainstay of fabrication of semi-conductor devices, integrated circuits and micro electromechanical devices. Sputter deposition using ion-beam offers significant advantages in the density, crystallinity, and grain size and thickness control of deposited films. The intervention of the beam in the coating process through shallow atomic mixing, ballistic effects of ion impact and surface migration also improves the adhesion and surface smoothness of films. Ion impacts also activate the surfaces by desorbing surface contaminants that interfere with adhesion and adversely affect coating properties. Ion impacts promote a very high “nucleation density” and a growth mechanism with minimal dependence on surface diffusion. The ions are essentially implanted into the first few atomic monolayers near the surface, so that the coating thickness increases by a process often referred to as “subplantation”. This situation is ideal for producing very thin coatings with excellent surface coverage. Additionally, the ion impacts result in coating material densification and extremely low surface roughness.

Free charges can be separated at sheaths and boundaries of quasineutral plasma. A conformal ion rich sheath develops around any object immersed in plasma and biased to potentials negative with respect to the plasma potential. We have seen earlier that the existence of an ion rich sheath implies that the ions enter this sheath from the plasma with the $\{kT_e/eM\}^{1/2}$ corresponding to an energy $kT_e/2e$. Under equilibrium conditions, the ion sheath delivers an ion flux to the electrode at a rate determined by the flow of ions into the sheath from the pre-sheath, which is usually at the Bohm velocity v_B. Thus, the ion current density drawn to this electrode can be written as:

$$j = nev_B$$

Flow of particles in space charge filled regions between electrodes was first modelled by Child who showed that the resultant space charge limited current is:

$$j = (4_o/9)\,(2e/m)^{1/2}\,V^{3/2}/\,d^2$$

Here $_o$ is the permittivity of free space, e is the charge on the particle and m its mass and d is the separation between the electrodes. This formula can be applied to both ion and electron sheaths. The fact that the current entering the sheath and the current drawn by the electrode must be equal determines the equilibrium thickness d of the sheath. If the voltage applied to the electrode is made more and more negative, the kinetic energy of the ions reaching the electrode increases in the absence of collisions within the sheath.

In many cases beams would be required at a remote location, physically separated from the plasma. An aperture of proper shape and size on the electrode can be used to extract part of the beam falling on the electrode. This is the essence of beam extraction from plasmas and the principle is qualitatively illustrated in Fig.4.10.

The plasma sources from which useful ion beams are extracted possess the following characteristics:

An ion flux density of typically a few tenths of amperes per cm^2

Uniformity in space and time (< 10%)

High content of atomic ions (more than 80%)

Low content of impurity ions;

Reasonable efficiency for the consumption of electrical energy and gas.

Industrially relevant ion beam sources can be divided into two categories; gridded and grid-less.

The actual formation of the ion beam occurs through electrostatic extraction and acceleration of the ions to the desired energy [Kaufman 1990]. Conventionally this is achieved by an arrangement of three or four metallic electrodes, insulated from each other, as shown schematically in the figure. In many sources a number of such beamlets merge to form the total beam. The role of the negative biased electrode, called the 'suppresser' or 'negative' or 'decel' electrode, is mainly to prevent electrons in the plasma in the post extraction region from being accelerated back into the electrode or into the source plasma. Furthermore, the decel electrode exerts an electrostatic divergent lens effect upon the ion beam. Here, the correct design of the extraction system plays an important role in the overall performance of the injection system, because there is no way of controlling the beam once it is ejected. Hence in contrast to atomic or nuclear physics accelerators the primary positive or negative ion beam must receive its final identity at the point of extraction.

The ions are emitted from a curved plasma surface, which has no fixed boundary. The curvature is determined by the self-consistent space charge limited flow of ions. For a given extraction geometry there is an optimum match between the ion flux density delivered by the plasma generator and the electrostatic potential V. i.e. an optimum perveance such that the resulting plasma curvature yields a minimum beam divergence. Calculations show that the divergence should go through zero at optimum perveance and increase linearly with perveance below and above the optimum. Because the matching condition for optimum beam divergence has to be met in every single aperture, the plasma generator has to produce an ion flux density, which is reasonably uniform in space and time. Non-uniformity larger than 10 per cent usually leads to a degradation of beam divergence.

Gridded ion extraction sources can be developed from most low pressure plasma sources. In an arc discharge source, electrons are emitted from a hot cathode with energy of typically 100 eV. Ionisation of the gas molecules leads to plasma formation. Numerous configurations, differing in the way of optimising the ionisation efficiency of the fast electrons have evolved over the last 25 years. The so-called bucket source, in which the arc plasma confinement is enhanced by means of a multicusp magnetic field (about 0.1 T) produced by rows of permanent magnets surrounding the source is a common configuration. The RF source utilises an oscillating electric field, generally induced by a RF coil, for the necessary acceleration of electrons in order to create the source plasma. RF sources have many advantages over the arc sources, such as long lifetime due to the absence of filaments, better control of the extracted ion current due to the direct response of the ion density in the source to changes of the RF input power etc.

Demands for improved ease of maintenance and higher beam currents for enhanced processing rates have driven the development of less complex, gridless ion-beam sources. Gridless sources [Kaufman 1985, Zharinov 1967] are simpler in design and do not suffer the space-charge-limit effect which limits the ion-beam current in for gridded sources. In addition, the gridless ion sources can also be operated without filaments, allowing the use of reactive gases that are incompatible with hot filaments. Furthermore, the ability to operate without grids or filaments increases overall process throughput by eliminating maintenance associated with these components.

The concept of plasma acceleration based on electric drift of charged particles was published by Sekel et. al in 1962 [Sekel 1962]. This concept was further developed in the Soviet Union for application in space propulsion. The modern Hall accelerator is, thus, another gift of space technology to plasma processing.

Coaxial Hall accelerator [Fig. 4.11] consists of an insulating channel, an anode, a magnetic circuit, which generates a radial magnetic field in the channel and an external cathode. The radial magnetic field lines form equi-potential surfaces. The magnitude of the field is approximately 200 gauss, strong enough to trap the electrons by causing them to spiral around the field lines. In the proper operating regime of such a device the electron Hall parameter (which is defined as the ratio of electron gyro frequency to electron collision frequency: = □□□) is larger than unity and the electron Larmor radius is small compared to a typical channel dimension, i.e. the electrons are magnetized. On the other hand, the Larmor radius of the much heavier ions is larger than the channel dimension and so they are not practically affected by the magnetic field. Under the influence of the axial electric and radial magnetic fields the electrons drift in the azimuthal direction (azimuthal Hall current). The trapped electron cloud serves as a virtual cathode.

Due to collisions, electrons diffuse across the magnetic field towards the anode, gaining thermal energy sufficient for ionisation of the gas atoms emerging from the anode. Axial electron mobility, which is controlled by the magnetic field profile, determines the electric potential drop. The magnetic field is minimum near the anode and increases towards the channel exit. As a result, most of the potential drop is concentrated near the exit. Consequently, it is expected that effective acceleration will start downstream the region where a substantial fraction of the flow is ionised and will take place along a short distance near the exit, thus maximizing the utilization of the electric potential for acceleration and minimizing ion losses due to wall collisions.

The ions, too heavy to be affected by the field, continue their journey through the virtual cathode. Since the ions are accelerated in quasi-neutral plasma there is no space charge limitation on current.

The end-Hall source has a cylindrical configuration with no inner parts of the channel and magnetic circuit. The magnetic field is similar to the fringing field of a solenoid. The electrons rotate along closed drift trajectories in the ExB direction, similar to coaxial Hall accelerators. Since the magnetic field of end Hall thrusters has a strong axial component, there appears a radial electric field, which produces a large beam divergence. Also, since these sources employ metal channel walls, the electron transport towards the anode can be enhanced by hot electrons, which are not cooled down by secondary emission. End Hall accelerator is thus typically characterised by a larger discharge current than coaxial thrusters are.

By comparison with gridded sources, the ion-beam energy obtained from a gridless source is low (<150 eV). In addition, the ion energy distribution is wide because the same DC voltage used to maintain the plasma also repels and accelerates the ions to form the ion beam. Since the local voltage falls off with distance from the anode, ions that form further from the anode are repelled by a lower potential and thus achieve a lower energy. In addition, the gridless sources have some interdependence of the main source operating parameters, i.e. anode voltage, beam current, magnetic field, and gas flow.

Sputter Generation of Metal Vapour Flux

Surface of a plasma container is the sink for charged particles, being continuously bombarded by electrons, ions and energetic neutrals. A process that is associated with this is the liberation of metallic atoms from the surface by sputtering [Carter 1968]. Controlled sputtering using energetic ions can be used to deposit thin films of materials.

Physical sputtering is a relatively violent (on an atomic-scale) process in which an energetic particle strikes a solid, resulting in the emission of one or more substrate atoms from the solid. This is very much like a stationary array of billiard balls being scattered by a fast ball shot into the array. In this model, the cue ball is the incoming ion or high-speed atom, the stationary balls (prior to being struck by the cue ball) are the sputter targets and the balls in motion (after being struck by the cue ball) are the sputtered atoms.

The sputtering process is characterised by a parameter termed yield being the ratio of the number of emitted particles to the number of incident ones. The yields for Argon ion bombardment of most materials range from 0.1 to about 5, with the majority of materials in the 0.5-2 range [Fig. 4.12]. The yield is an average number, including not only the emission rates from a number of different crystalline orientations, but, on the atomic scale, a number of different impact points for the incident particles. The yields are energy-dependent in a roughly linear fashion.

At relatively low energies, the incident particles do not have adequate energy to break atomic bonds of the surface atoms, and the bombardment process could result in simply heating the surface, desorbing a few lightly bound gas atoms, perhaps inducing a chemical reaction at the sample surface, or nothing at all.

Sputtering begins above an energy threshold of the order of a few tens of eV. Physical sputtering is like sublimation - a change of state from solid directly to a gas without first liquefaction - hence the threshold energy is related to the heat of sublimation. Most commercial sputter deposition and etch processes are performed in this region. The low energy segment is used in sputter etching. The deposition rate being approximately proportional to power, the low energy range can be used when precise thickness control is essential.

At relatively high incident energies, the bombarding particles travel deeply into the bulk of the substrate and may cause deep-level disruptions in the physical structure, but few if any surface atoms are released. At moderate energies, typically in the range from several hundred eV through several keV, the incident particle can cause substantial numbers of near-surface broken bonds, atomic dislocations, and ejection or sputtering of atoms. This range includes the upper reaches of the "weak screening" scattering and the transition into the Rutherford (nuclei-nuclei) scattering region.

The emission profile for the sputtered atoms is characterised by a cosine distribution for most materials [Fig. 4.13]. This means that the emission rate at some angle other than normal is equal to the normal incidence yield times the cosine of the angle from the normal. There is an additional angular dependence of the sputter yield relative to the incoming ion. Not all materials have the same angular distribution of sputtered material. To add to the complexity, energy dependence of the yield is also different for each material. This causes problems in sputtering alloy films where a precise composition is critical.

The cosine like angular emission profile of the sputtered atoms, coupled with the extended area of plasma ion flux and perhaps some in-flight gas scattering, implies that the depositing flux of sputtered atoms has a very broad, almost isotropic nature. This can be extremely useful in depositing films on unusual, non-planar surfaces, over steps or ledges, and on the sides of features. As a result, sputter-deposited films are smoother than the underlying surface.

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Table I: Energies of species compared to chemical bond energies. All energies in eV

Species	Energy	Chemical Bonds	Enthalpy
Electrons	0-20	CH	4.3 (414) kJ/mole
Ions	0-2	CN	2.9 (280)
Metastables	0-20	CCl	3.4 (330)
Photons	3-10	CF	4.4 (426)
		CO	8.0 (774)
		CC	3.4 (330)
		CC	6.1 (590)

Figures

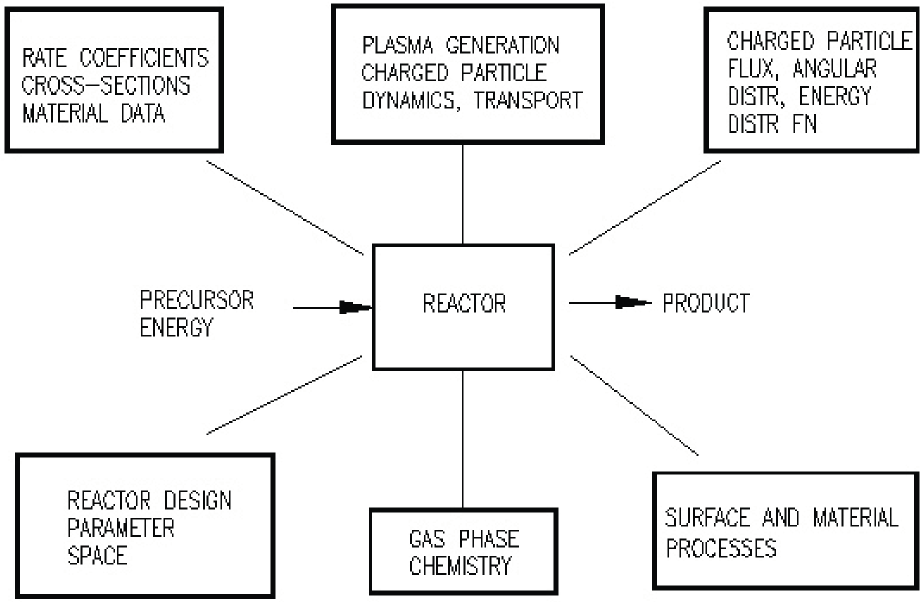

Fig. 4.1. Concept of the plasma-processing reactor illustrating the complex relationship between plasma and gas parameters and processes to the manufacturing proces

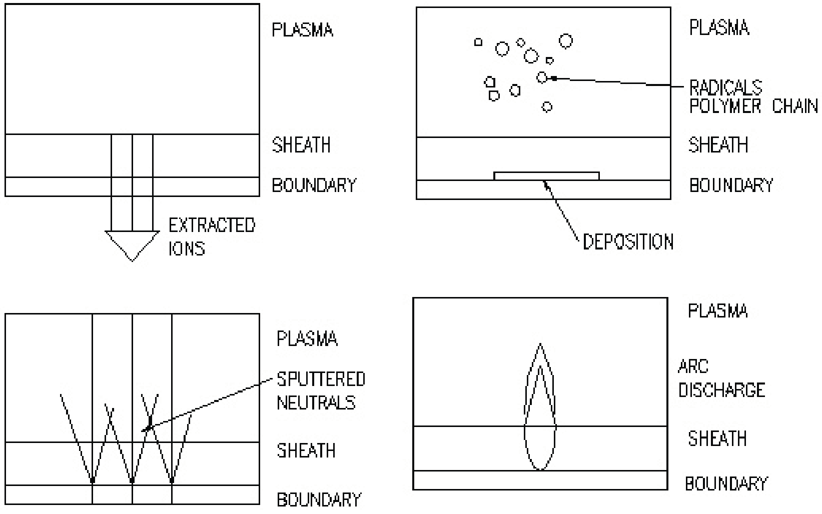

Fig. 4.2. The four phenomena in plasmas enabling plasma to become an industrial tool: production of energetic particles, plasma chemical reactions, generation of neutral atoms and plasma as a heat source

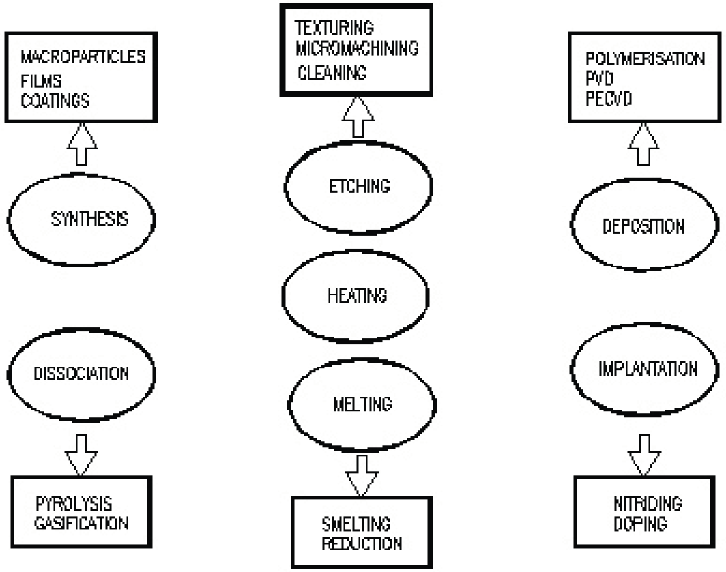

Fig. 4.3. The ‘seven pillars’ of plasma processing, which utilizes the four basic phenomena

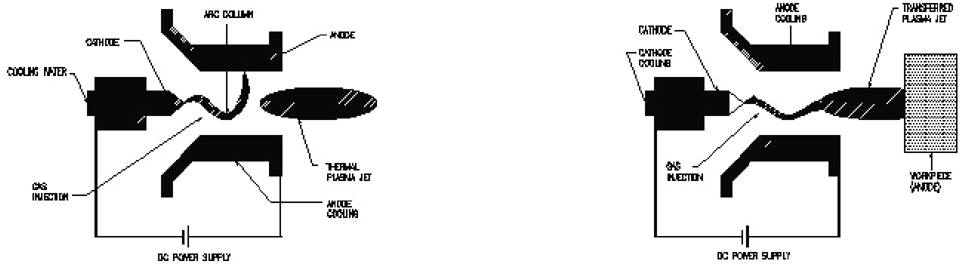

Fig. 4.4. Schematic diagram of two fundamental types of plasma torches (a) dc transferred torch (b) dc non-transferred torch

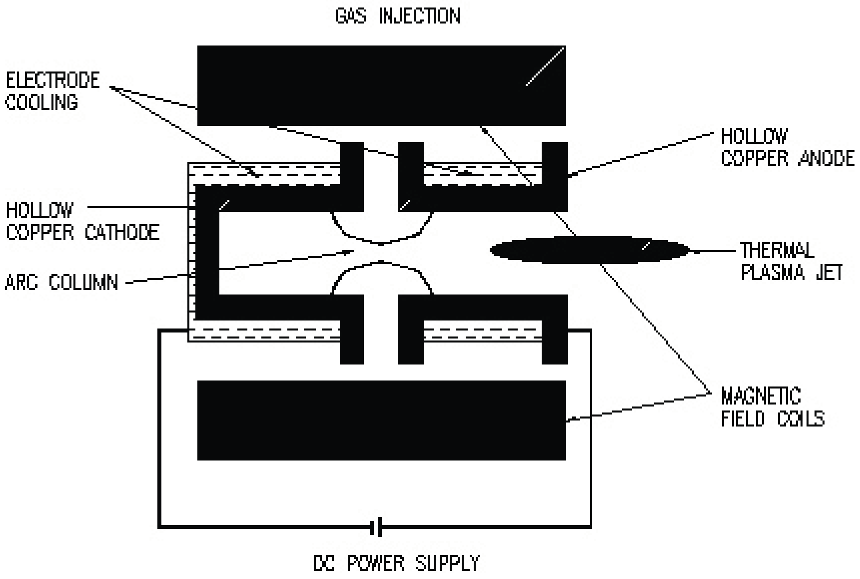

Fig. 4.5. Torch with hollow cathode

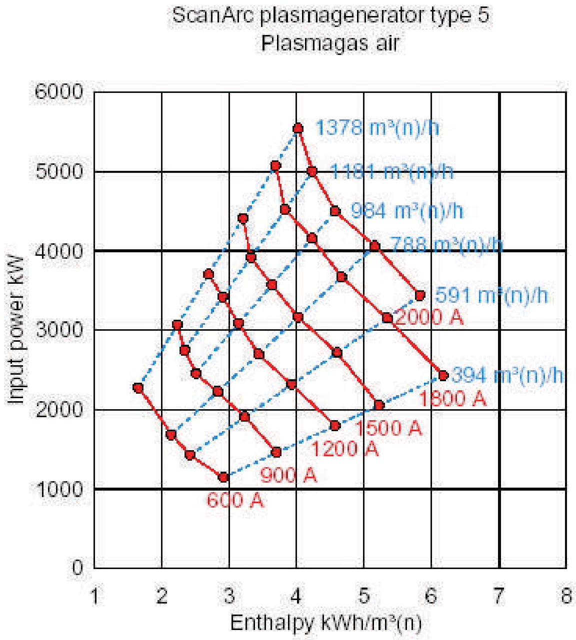

Fig. 4.6. Relationship between input power and enthalpy for a commercial plasma torch (Figure courtesy of ScanArc Plasma Technologies)

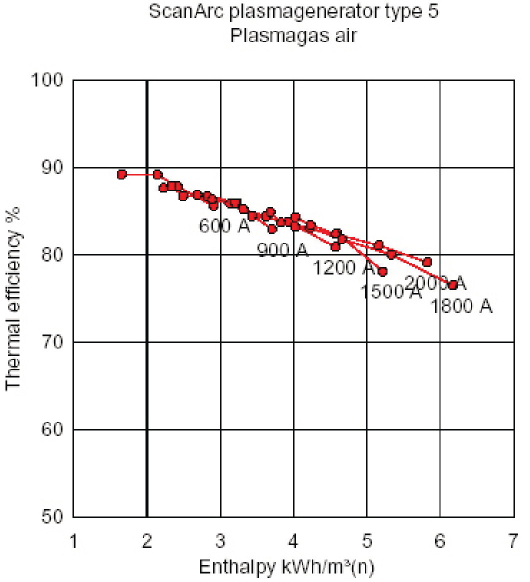

Fig.4.7. Thermal efficiency of a torch as a function of enthalpy (Figure courtesy of ScanArc Plasma Technologies)

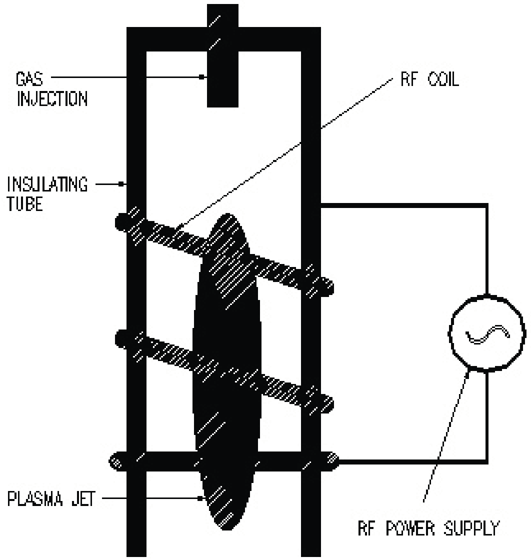

Fig. 4.8. The inductive plasma torch

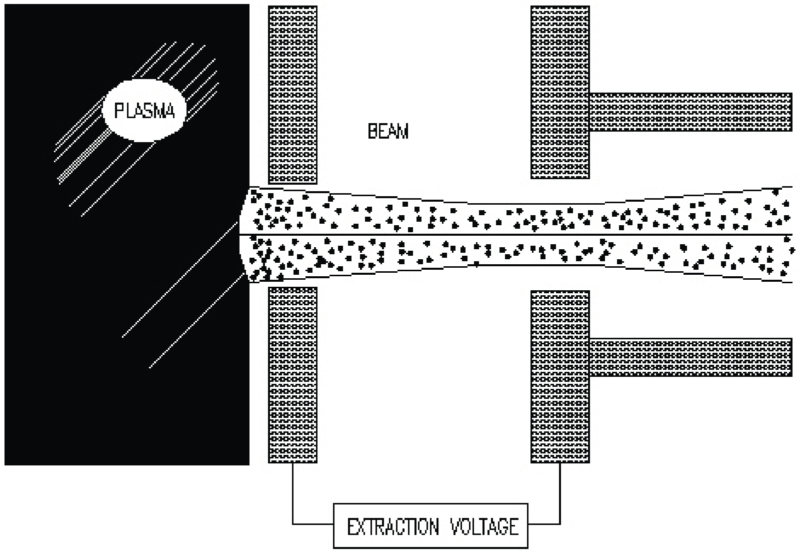

Fig. 4.10. Charged particles can be extracted from plasma using appropriately designed electrodes

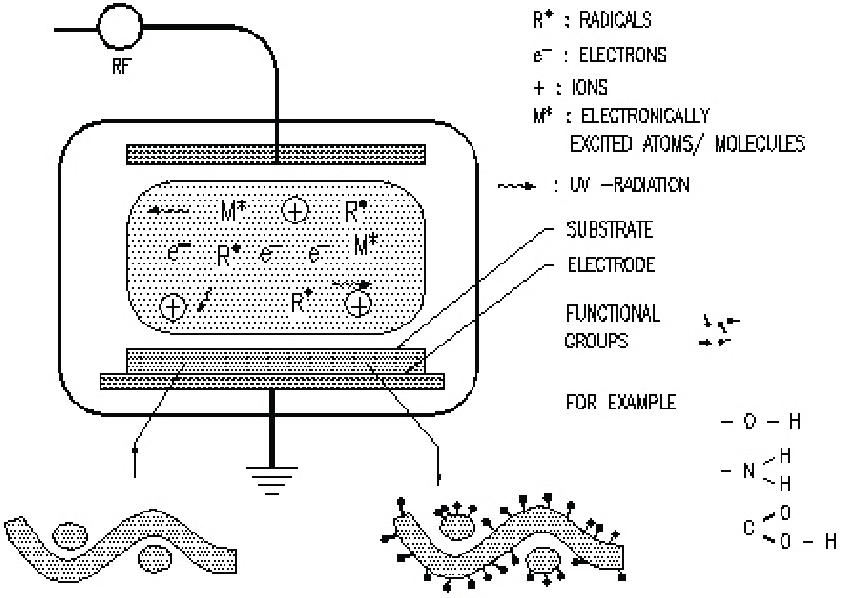

Fig. 4.9. Schematic illustration of the plasma polymerisation process

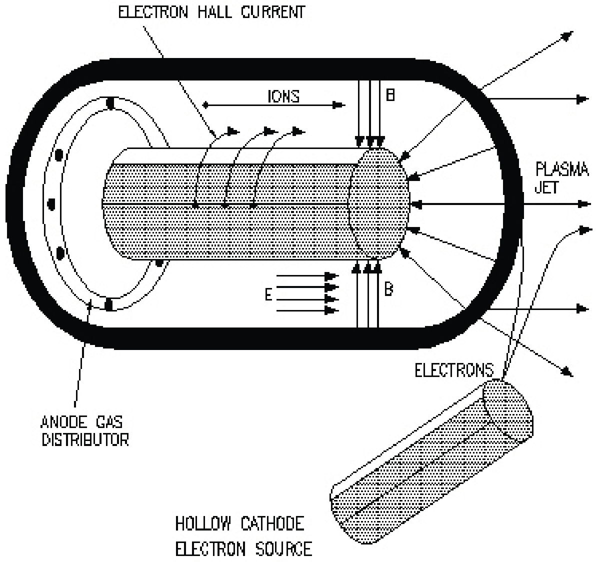

Fig. 4.11. Coaxial Hall accelerator utilises the electric field generated by azimuthally drifting electrons trapped in a radial magnetic field

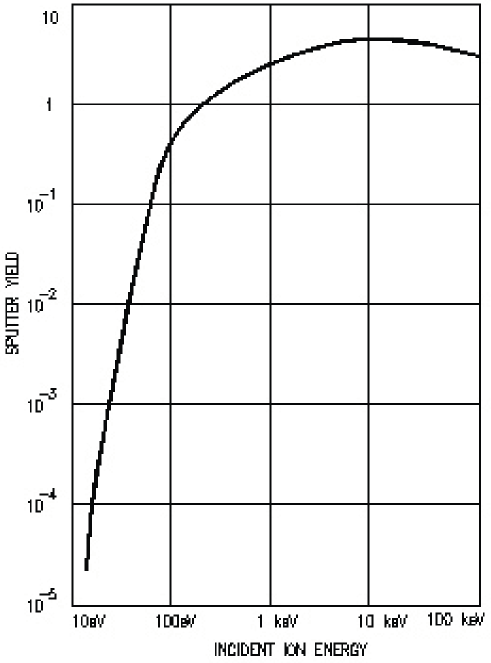

Fig. 4.12. Sputter yield as a function of the energy of the incident particles

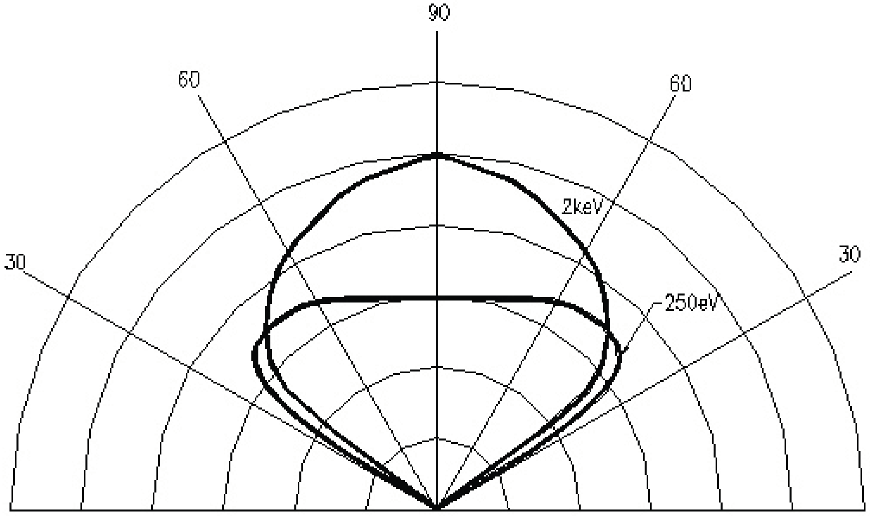

Fig. 4.13. Angular distribution of sputtered particles follows a cosine law

5. The Nitride Shield

Surface Alloying by Diffusion Treatments

When steel surfaces at elevated temperature are exposed to nitrogen plasma, the nitrogen atoms dissolve in the metal and form nitrides of the alloying elements. This is the plasma equivalent of a thermochemical diffusion process called nitriding. The layer of surface nitrides form a hard shield against wear, corrosion etc. In this chapter, we shall discuss the plasma nitriding process and reactors and describe a variety of industrial products, which benefit from nitriding.

The Wear Problem

Legends speak of Damascus steel, used to make swords of great sharpness. The art of making this steel was lost long ago. The distinctive surface patterns on these blades result from a carbide-banding phenomenon [Smith 1983] produced by the micro segregation of carbide-forming elements present in the ingots from which the blades were forged. The most common use of these steels was for making swords and daggers. The name Damascus apparently originated with these steels. The steel itself was produced not in Damascus, but in India and became known in English literature in the early 19th century as wootz steel.

Surface properties determine the performance of many engineering components, with the bulk acting primarily as a template to provide core properties like strength and toughness. Alloying of a thin surface layer is possible by doping it with atoms of Nitrogen, Carbon and Boron, which can chemically react with the atoms of the solid and form nitrides, carbides or borides respectively [Hoffmann 1992]. These elements can be added to the surface of a workpiece by a process called thermochemical diffusion in which activated gases are brought into direct contact with the surface held at an elevated temperature. The different categories of thermochemical diffusion treatment are given in Fig. 5.1. The alloyed layer exhibits many desirable properties. Surface hardness is one such property, essential to machine parts like gears, racks, pinions, sprockets, plastic moulding dies and extruder screws etc. However, the processes are not confined to interstitial diffusion; metallic substitutional elements or metalloids are used in processes such as chromising, aluminising and siliconizing. The parameter space and the depth of treatment of various diffusion processes are given in Fig. 5.2.

Diffusion treatments fall into two basic categories: low temperature treatments within the ferritic range and high temperature treatments in the austenitic range. Ferritic processes include gas nitriding and nitrocarburizing done in the 500-550 °C range. Salt baths (cyanides or non-toxic cyanate mixtures), endothermic ammonia gas mixtures, and methane or propane/ammonia/oxygen mixtures are employed. Typical case-depths are of the order of 250 microns on alloy steels. On low carbon mild steel, they can produce a thin 'compound layer' of the order of 10 microns thick which can improve both wear and corrosion resistance. The austenitic treatments are performed at temperatures near 900°C and produce case depths as large as several millimetres. They include carburizing employing solid (pack), liquid (salt bath) or gaseous media, carbo-nitriding and boronising. Such treatments produce greater surface growth and distortion. Thermochemical treatments involving diffusion of substitutional elements, chromium (chromising) or aluminium (aluminising) are often used for use at elevated temperatures on nickel-based super-alloys or nickel/chromium materials.

Nitrogen Interaction with Metal Surfaces

Gas-metal interaction starts with adsorption of a gas molecule at the metal surface [Mijiritskii 1973]. Once sorbed on the surface, the molecule can be dissociated or desorbed from the surface. The dissociation products can either be absorbed by the bulk of the metal or can recombine and desorb from the surface. The occurrence of these processes depends on the nature of the gas and metal involved, and on the temperature and pressure, as well as the cleanliness of the surface.

Interaction between Fe and Nitrogen gas is basically limited to the adsorption and desorption of the Nitrogen molecules. This is due to fact that the sticking coefficient on Iron for the dissociative adsorption of Nitrogen is very low; of the order of 10^{-7} to 10^{-6} seconds. The dissociation of N_2 at the α-Fe surface can be promoted by adding Hydrogen. In this case the formation of adsorbed N atoms takes place via surface reactions, which require a smaller activation.

$N_{2ads} + H_{2ads} \quad 2NH_{ads}$ (1.2)

$NH_{ads} \quad N_{ads} + H_{ads}$ (1.3)

Even in the presence of H_2 the surface reactions are still relatively slow, so that they determine the rate at which Nitrogen atoms are taken up by the metal. However, if NH_3 is used, then much larger quantities of atomic N are produced and subsequently taken up by α-Fe. The relevant reactions are:

NH_{3ads} $NH_{2ads} + H_{ads}$ (1.4)

NH_{2ads} $NH_{ads} + H_{ads}$ (1.5)

NH_{ads} $N_{ads} + H_{ads}$ (1.6)

The bulk metal can either absorb the adsorbed atomic N and H or two adsorbed N atoms can recombine to form a N_2 molecule and desorb from the surface. The various steps in nitrogen absorption by metallic surfaces are illustrated in Fig. 5.3.

Nitrogen can be taken up by Fe in appreciable amounts, determined by the temperature of the system and the partial pressure ratio of the gases in the mixture provided the gas is present at the metal surface in the form of atoms and bulk diffusion is sufficiently fast. Once absorbed, the small physical size of nitrogen (0.71 Å) enables them to fit snugly in the Iron lattice. The stress produced by the distortion of the lattice is supposed to increase the hardness.

Absorption of gas atoms leads to crystallographic phase transformations in metals. Incorporation of N atoms into the interstitial hollow sites causes elastic distortion of the Fe lattice resulting in the BCT structure (the α_{-} phase). At the $\alpha_{-}Fe_8N$ composition, the solubility limit of N in the BCT lattice of α_{-} reaches its maximum. Once the elastic energy barrier of the BCT phase is exceeded, a new interstitial phase γ' (gamma prime) is formed. The γ' phase has the fcc structure and, thus, provides larger interstitial sites so that lower strain energy needs to be provided for accommodation of N atoms. This phase has only a relatively small region of homogeneity around the composition Fe_4N. Further Nitrogen uptake leads eventually to a more nitrogen-rich Fe-nitride, known as the ε phase.

Once the phase formation has begun, a layer of gas-metal compound can be formed at the surface of the sample. This layer can alter the dissociation rate and serve as a diffusion barrier. Thus, the products of this process will influence the process of gas-metal interaction. In the specific case of Fe-nitriding, a porous Fe-nitride can be formed due to the simultaneous formation and decomposition of Fe-nitrides into Fe plus N_2. This happens because Fe-nitrides are metastable compounds with an enthalpy of formation, which is close to zero. The decomposition only takes place at temperatures above 500°C.

Plasma Nitriding

In plasma nitriding (also called ion nitriding) the plasma assists the nitrogen diffusion process through both surface and volume chemical reactions on the nitriding surface. The origins of this process can be traced back to the discovery by Lord Rayleigh that electrically dissociated nitrogen was very reactive compared to the inert gas. Technological application began with the work of Wehneldt and Berghaus [Berghaus 1939] in the 1930's who were successful in stabilising glow discharges for application to steel nitriding.

In the plasma nitriding process, a Nitrogen-Hydrogen gas mixture is converted into plasma by a glow discharge in which the work piece to be nitrided acts as the cathode. The plasma sheath surrounding a gear being nitrided is shown in Fig. 5.4a. The companion Fig. 5.4b shows a stack of components being immersed in the nitriding plasma. The efficiency of the plasma discharge in forming atomic Nitrogen or compounds like NH replaces the production of atomic nitrogen and NH by thermal dissociation of N_2 on the hot surface of the work in gas nitriding.

Why is ion nitriding in which a component is exposed to a much smaller concentration of Nitrogen containing species more effective than gas or salt bath nitriding where the densities are larger by a factor of a million? Why are plasma nitriding time scales much shorter than that of the gas process?

Many theories exist on the basic mechanism of plasma nitriding. Some assume the formation of iron nitrides in the gas phase as the precursor. According to Kolbel's hypothesis [Kolbel 1965], sputtered iron reacts with Nitrogen in the gas phase to form unstable FeN, which condenses on the surface and dissolves into stable iron nitrides like the phase $Fe_{2-3}N$ and the phase Fe_4N. Heterogeneous reactions of NH_x with iron leading to formation of iron nitride in the boundary layer, which decompose to release Nitrogen is considered possible. Application of a magnetic field can lower the pressure of the gas for nitriding. At this low pressure there is negligible back diffusion of the sputtered molecules to the surface, contradicting the condensation mechanism.

Another school assumes Nitrogen adsorption, penetration and reaction to form stable nitrides [Edenhofer 1974, Tibbets 1974]. In this case the case depth should be independent of the ion flux, which is inconsistent with experimental results. In a third approach, ionic Nitrogen is considered to dominate the process. Hudis [1973] led the view of the importance of ionised Nitrogen in the nitriding process and maintained that the accelerated nitriding is due to the bombardment of the work piece by ions.

Recent work with extensive plasma and surface diagnostics coupled with modelling is beginning to unravel the complexity of the nitriding process to some extent. Spectroscopic diagnostics [Szabo 1984] of nitriding plasmas show that molecular Nitrogen ions, vibrationally excited Nitrogen molecules and atomic Nitrogen are the species most relevant to the process. By using emission and absorption spectroscopy, Ricard et. al. [Ricard 1987] showed that N_2^+, the vibrational N_2 and neutral N species are most relevant for steel nitriding. Marchand et. al. showed that optimum nitriding takes place when the vibrational level is V= 46 [Marchand 1990].

Bokman and Tuler [Bokman 1981] have postulated that plasma nitriding is faster than gas nitriding due to the ion induced surface radiation damage and creation of vacancies to a depth of tens of atomic layers. The dependence of the case depth on ion flux is based on the diffusion of vacancy-ion pairs. The only stable ions within the metal surface are those, which are conjugated by electrostatic forces to the vacancies formed by ion bombardment. The vacancy-ion pairs migrate into the bulk by vacancy substitutional diffusion, in contrast to the interstitial mechanism for Nitrogen atom diffusion.

The role of hydrogen still remains an enigma in plasma nitriding. For transition metals, absorption of even small amounts of Hydrogen in the presence of a large number of vacancies at the surface causes the formation of exciton like Hydrogen vacancy surface states [Szasz 1989]. These are acceptor-like states with large correlation lengths that can assist in the capture of Nitrogen species from the gas phase into an adsorbed state. Ion damage and implantation could be a direct mechanism for the creation of Nitrogen vacancy pairs, while the chemical exchange of Hydrogen-Nitrogen species at the surface would be far more effective in their creation. Charge transfer into the exciton-like Hydrogen state weakens the molecular bond of the adsorbed N_2. Atomic Nitrogen then interacts with the metallic iron. Thus, Nitrogen and Hydrogen electronically exchange producing nascent adsorbed Hydrogen atoms and Nitrogen vacancy pairs. The latter diffuse into the bulk metals, while the former can cause new exciton like states. The vacancy-ion pairs migrate into the bulk by vacancy substitutional diffusion in contrast to the interstitial diffusion of atomic Nitrogen, which is slower.

Recently Sun and Bell developed a mathematical model to simulate the plasma nitriding process for low alloy steels [Sun 1997]. They considered the mass transfer from the plasma to the surface, the diffusion of Nitrogen in the ferrite, the precipitation of fine-scale alloy nitrides in the diffusion zone and the development of Fe_4N on the surface and generated reasonable agreement with experimental data.

Variants of Plasma Nitriding

Plasma nitriding is usually carried out in a pressure range of 3-10 mbar. At this pressure the plasma is in close contact with the substrate. For substrates with complex shapes, like surfaces with small grooves or threading, the local plasma parameters near the complex shape may vary. This modifies the electric field and hence the ion concentration and energy of bombardment of ions on such regions. Highly collisional sheaths associated with conventional plasma nitriding results in low ion energy, insufficient for activating oxide rich surfaces like those of stainless steels. Both these effects may lead to overheating the region leading to different nitriding properties compared to the rest of the substrate. In the abnormal glow discharge used for conventional plasma nitriding, it is not possible to modify one parameter independent of others as all are coupled with each other.

Low-pressure plasmas have been exploited to overcome the above drawbacks. At pressures below 10 Pa, an abnormal glow discharge cannot be used. Plasma generation is realised by radio-frequency excitation [Meletis 1993], microwaves or electron impact ionisation by energetic electrons emitted from thermionic filaments. These low-pressure plasmas diffuse throughout the treatment chamber and are known to contain a large number of active species, which increase the nitriding efficiency. In RF plasma nitriding the plasma generation is separated from substrate bias, which allows independent control of the ion energy and flux at the substrate surface. Since the operating pressures are low, the gas consumption is also reduced.

In the radical nitriding technique, a low energy DC glow discharge effectively produces NH radicals and their high activity is used for nitriding. An external heater heats up the work piece. This is almost an electrical analogue of the gas nitriding process. It is claimed that precise control of the surface topology is possible and that it is possible to select whether a compound layer is formed or not. Thickness of compound layer and depth of diffusion layer are also claimed to be controllable with the surface texture unchanged after this treatment. Areas such as narrow slits and holes can be treated with ease in this process.

Conventional plasma-nitriding techniques use an abnormal glow discharge, either dc or pulsed. They perform well when nitriding low-alloy and tool steels, but they are less successful with stainless steel, particularly those grades with an austenitic structure. The high treatment temperature in the nitriding processes causes precipitation of CrN, resulting in surfaces that are hard and resistant to wear but suffer from poor corrosion properties. The use of lower treatment temperatures and low-pressure discharges has been found to be successful in addressing this problem. The modified layer produced using such processes with low temperature and low-pressure discharges contain a Nitrogen-rich phase called expanded austenite.

Properties of the Nitrided Case

The nitrided case consists of the compound layer at the surface overlaying the diffusion zone as shown in the photograph in Fig. 5.5a and 5.5b. The compound layer has a thickness in the range of 0 to 20 µm, whereas the diffusion zone can be as thick as 0.7 mm. The properties of the layers are functions of the steel quality, treatment parameters, temperature, duration and gas environment. Plasma nitriding process can produce Fe_4N or $Fe_{2-3}N$ type layers or mixed layers over a broad range of layer thickness as well as completely avoid a compound layer.

The compound zone is commonly called white layer due to its appearance after the nital etch. It has high hardness and good resistance to wear and deformation. The primary constituents are Iron-Nitrogen inter-metallic compounds like Fe_4N (□□phase) and $Fe_{2-3}N$ (□□phase). Excess concentration of Hydrogen catalyses the □' phase. The compound zone can be controlled in thickness or completely eliminated by choice of gas composition and temperature. A ductile Fe_4N compound layer is sometimes recommended to avoid wear whereas a Fe_{2-3} N compound layer sometimes with Fe_3O_4 has good resistance to wear and corrosion.

The diffusion zone is located immediately below compound zone. This is composed of Nitrogen in interstitial solution in the ferrous matrix in combination with nitride dispersions. It can be established almost clean of nitride precipitation and nitriding along grain boundaries. The hardness of the diffusion zone is determined by nitride-forming elements such as Chromium, Molybdenum, Aluminium, Titanium, Manganese and Tungsten. The depth of the diffusion zone is generally a function of duration and temperature of the process, the alloying elements and the method of presenting atomic nitrogen to the surface. High nitriding temperatures promote the formation of large, coarse distributed nitrides, whereas low temperatures promote the formation of finely dispersed nitrides. Slow cooling rates after nitriding, annealing treatments or heating by stressing the parts favours distribution, growth and change in the nitride structure. Either increasing the temperature or the process time can increase the nitriding depth. Increasing the content of nitride forming elements increases the hardness of the surface layer and decreases the nitriding depth. Both the hardness and depth parameters depend on the extent of non-ferrous nitride formation [Fig. 5.6].

Improvement of Mechanical properties

The diffusion zone determines the fatigue properties of nitrided components. Work pieces with nitrided cases prove effective under dynamic stresses. In a ferrous material, Nitrogen will exist within the lattice structure as individual, separate atoms upto the limit of solubility of Nitrogen in Iron. Precipitates of the nitrides form as the concentration of Nitrogen approaches the limit of solubility. The mechanism by which the hardness is increased is believed to be due to the distortion of the lattice structure when nitrogen penetrates it.

Plasma nitrided surfaces have less porosity in contrast to conventionally nitrided surfaces, which have a highly porous structure. In certain wear applications in which a fretting wear is encountered, it is sometimes desirable to impart some porosity to the surface, as porous layers are known to retain lubricants in the contact zones of opposing wear surfaces. Porosity can be imparted through the addition of ammonia to the gas composition. Nitriding of high-speed tools is done to increase the wear resistance of the cutting edge and reduce the tendency of the work to weld to the cutting edge. These factors depend on whether the work piece is soft and sticky, such as mild steel, or hard and abrasive, such as tool steel. Also, mechanical strain due to tensile, compressive, bending, shear, and torsion stresses act on the part. Typically, nitriding is done to enhance sliding wear resistance and is usually a poor choice for heavy-impact wear.

Nitriding is considered a low or no-growth treatment, ideal for most production applications like casting forging and machining. The prior mechanical working and heat treatment are the source of distortion in a workpiece. If they have been properly annealed for stress relieving at a temperature of at least 50° above the nitriding temperature, the treatment should involve no distortion. Long thin parts can be hung in the fixtures to relieve the stress due to self-weight at the treatment temperatures. Under these conditions, distortion can be held to a minimum.

Sputtering can cause an increase in roughness of a surface, though to a lesser extent than in most conventional case hardening processes. A typical range in increase in surface roughness is 0.2 - 0.5 microns. Simple polishing can restore the original finish.

Plasma Nitriding Reactors

Plasma nitriding reactor technology has developed along three directions. The most obvious of these has been in scale, capacity and other, essentially mechanical attributes. From the one-foot chamber of Berghaus, giant Megawatts systems have become common. The cold wall has been replaced with hot walls or with reactors with efficient heat confinement to improve overall energy economy. Besides, auxiliary heating speeds up the cycle. Plasma production systems incorporate pulsing and pre-detection of arcing to prevent arcing-induced damage to the work piece. The process is run through computer based automated systems.

Plasma nitriding reactors are conceptually similar to vacuum heat treatment equipment [Fig.5.7]. They are usually built around a bell type vacuum enclosure heated using internal or external resistance heating elements and insulated with lightweight thermal insulators to prevent heat loss. Typically, the auxiliary heater provides 50 per cent of the energy required for reaching the nitriding temperature. The rest is supplemented by plasma heating. The base has electrically insulated hearth, which supports the work to be nitrided. The vacuum pumping system is designed to have large throughput for quick evacuation and purging with inert gases or Nitrogen to condition the vacuum vessel. The process gases are introduced into the chamber by mass flow controllers and the overall pressure is maintained using conductance control valves. Large chambers also employ internal gas agitators to ensure proper mixing and circulation of the gas inside the chamber.

A typical plasma nitriding process cycle starts with uniform loading the parts on the reactor hearth, with a gap of few centimetres. Since the surface to volume ratio determines the plasma heating, the distribution of parts on the hearth requires considerable care to ensure uniform heating over the volume. Heating and degassing using the auxiliary heaters follows evacuation to a pressure better than a millitorr.

Application of voltages of the order of 300 V or above on the workpiece produces the glow discharge. Near the cathode, there are relatively dark regions called Aston and Crooke's dark space, which is identical to the cathode sheath where most of the voltage applied between the cathode and the anode, appears. The electrons originating from the cathode are accelerated in this region. Beyond this is a region of intense brightness, where gas is ionised by the electrons and emit the characteristic spectral colour. The negative glow region merges into the positive column, which is the quasineutral plasma region with low electric field. The positive column connects to the anode through the anode glow and the anode dark space. The anode glow can be uniform across the anode surface or can be spots of luminous spheres.

The electron temperature is determined by the balance between power dissipated in the discharge and power loss to the walls through the drift of charged particles and neutral gas convection. The electron density in a glow discharge is of the order of 10^8 to 10^{11} cm^{-3}, for pressures in the Torr range. At this pressure the neutral density is in the range of 10^{16} to 10^{17} cm^{-3}. The degree of ionisation of the gas is thus 10^{-8} to 10^{-7}. The electron temperatures are in the range of 1-3 eV, which corresponds to thermodynamically equilibrium ionisation of 10^{-2} or higher. This inconsistency is because the glow discharge is a non-equilibrium phenomenon where the ionisation is not balanced by radiative recombination.

Sputter cleaning of the surface by the discharge plasma is the next step aimed at removing organic traces and the oxide layer of the surface, which inhibits N nitrogen penetration. Following this, the power is boosted so that an average current density of 2-3 milliampere/cm^2 is obtained and the surface is heated to the required nitriding temperature. After the process is over, the discharge is terminated and the workpieces cooled down, usually using forced Nitrogen circulation.

The glow seam can be interrupted to mask areas in where treatment is not desired. The masking is accomplished quickly and inexpensively using mechanical masking techniques. Results are comparable in effectiveness to expensive and time-consuming copperplate masking operations used in gas nitriding. Stainless steel foil can also be used. Mechanical masks are selected to fit closely to avoid hollow cathode effect in the gap.

A major area of development of plasma nitriding technology has been in the power electronics and plasma formation techniques, as well as vacuum chamber design, both of which have implications on the process aspect. The early devices used a steady dc voltage to excite the plasma, and the discharge was stabilised at the abnormal glow phase by using an external ballast resistor. This is not electrically efficient as a large fraction of the power is dissipated in the ballast resistor. With advent of fast power electronics, kilovolt pulse trains became available for plasma excitation. The pulse duration can be of the order of a few tens of microseconds. This inhibits the glow to arc transition. Hollow cathode effect, which results in localised heating resulting in damage in the vicinity of small holes etc, disappears with the pulse train nitriding. By changing the duty cycle, the pulse train can be effectively used to control work temperature. With the advent of solid-state devices like the insulated gate bipolar transistors, compact high power pulsers are readily engineered.

Modern plasma nitriding reactors [Fig. 5.8 a, b] are substantially automated with menu driven process phases. Industrial PCs or programmable logic controllers are used. A third direction of development involving both process and reactor technologies has been towards duplex reactors, which combine more than one form of surface engineering treatment. Plasma nitriding and carburisation in single reactors have already been commercialised. Pre-nitriding prior to PVD deposition of titanium nitride to improve the adhesion of the nitride layer is another example of a duplex process.

Other Thermochemical Diffusion Treatments

Plasma Nitrocarburizing is performed in Nitrogen - Hydrogen gas mixture with Methane or Carbon dioxide providing the Carbon. The surface modification manifests as a nitrogen rich compound layer about 2 to 10 m thick, overlying a sub-surface diffusion layer, which may be several hundreds of microns thick. The compound layer improves the wear and corrosion resistance while the diffusion layer contributes to the enhancement of fatigue resistance.

Despite considerable research, plasma carburising is yet to gain the same level of commercial popularity as plasma nitriding. The process is usually carried out in Argon-Hydrogen atmospheres with CH_4 or C_3H_8 as reactants. The process requires an auxiliary heating system due to the higher treatment temperatures, while the plasma is mainly used for activating the gas mixture. Fast quenching using Helium is useful in stabilizing the carburised layer. The advantages of plasma carburizing over its conventional counterpart are enhanced mass transfer of Carbon and consequent increase of processing rate, and the prevention of oxidation including intergranular oxidation [Grube 1979]

Plasma diffusion treatment before and after vapour deposition hard coating has become possible [Matthews 1995] with the availability of low-pressure plasma nitriding systems. Prenitriding of tool steel substrates can provide substantial increase in coating adhesion. This improvement is attributed to improved load support from the hardened substrate.

The need for hardened but cheaper PVD coatings has motivated the deposition of such coatings on surfaces pre-deposited with Nitrogen content. Both coating and diffusion treatment is performed below 400°C to prevent the grain-boundary segregation and precipitation effects and to retain corrosion resistance. Coatings with increasing nitrogen content typically show surface hardness of 1500 Hk 25 g (Knoop hardness at 25 gm load), similar to that of conventionally plasma nitrided Stainless Steel. But the important new factor is that the graded Nitrogen content in the coating minimises internal stresses and improves toughness. Plasma nitriding of nitrogen-doped coatings increases surface hardness up to 2500 Hk 25 g, which approaches the hardness of PVD TiN coatings.

Since the beginning of 1980s, processes, which combine nitriding and nitrocarburising with oxidative processes with various trade names such as PLASOX, IONIT OX, have become popular [Dawes 1985]. The formation of the oxide layer is influenced by the outer porosity of the compound layer of the nitrided surface. With a pore system open to the outside, the inner surfaces of the pores and the pores themselves will be totally covered and filled by the oxide. With an open pore system, Oxygen penetrates into the compound layer. The Nitrogen austenite layer below the compound layer changes into Nitrogen-Bainite with improved toughness and wear properties [Hoppe 1998]. In the IONIT process, a gray oxide layer with 1-3 micron thickness is formed above the □-carbonitride layer with boundary between oxide-nitride layers deeply structured. Different oxidizing processes are listed in Table I.

Industrial Applications

Plasma Nitriding as an industrial process has many advantages. The cycle times for nitridable steels are typically one third to a half of conventional gas nitriding, thereby reducing operating costs. Reduced distortion, masking with simple mechanical masks and dispensing of finish grinding improve productivity. Improvement in metallurgical properties often enabling cheap materials to replace costly ones of lower cost is another attraction. Hard wear resistant surfaces can be generated without brittleness or causing spalling or galling usually associated with conventional nitriding. It can provide uniform case on complex geometry. Since the process is free of toxic salts or toxic gases, it is environmentally friendly. A typical gallery of plasma nitridable steels is given in Table 5.2. Industrial components routinely plasma nitrided are shown in Fig. 5.9.

Premixed gases are commercially available for producing specific properties. With a composition of generally less than 5 per cent nitrogen and the balance of inert gas (typically Hydrogen or Argon) compound layer of iron nitrides can be avoided.

A mixture of 15-30 per cent Nitrogen and the balance of inert gas is called □' gas which forms a very thin compound layer of predominantly monophase □' crystal structure (Fe_4N) irrespective of the process duration. Longer process times develop deeper diffusion layer and the higher temperatures increases the thickness of the compound layer. Typically, this layer would be used on nitriding steels (Nitralloy 135 or 4140).

Epsilon gas consists of 60-70 per cent Nitrogen, 1-3 per cent Methane and the balance made up of an inert gas. This gas composition tends to form preferentially monophase □□crystal structure ($Fe_{2-3}N$). The compound layer thickness as well as the case depth increases with treatment time. In many applications the □□compound layer of only 5 to

10 micron is sufficient for wear resistant applications. Higher process temperatures will result in thicker compound layers being formed in shorter periods of time. This gas composition is traditionally used on materials that have no alloy constituents to form a diffused nitride precipitate case structure.

Plastic Manufacturing Components

Developments in the plastic industry are accelerating at a great speed, and newer materials for products as well as for tools are being put to use. Plastic moulds are normally high-cost and complicated components, consisting of many parts in relative motion to each other and to the plastic material. Abrasion, adhesion, corrosion, sticking, and fatigue are common operation problems, and several types of wear can be observed at the same time. The most critical components that are subjected to wear during plastic processing are injection moulds, plastic moulds, screws and barrels. Most commonly used steels for manufacturing plastic moulds and their mould life is shown in Table 5.3 [Medical Plastics Data Service, July 1999].

Most of these components are subjected to high injection pressures and to erosive/corrosive plastic material during processing. As a result, the lifetime of the moulds is limited by the wear properties of the die material. Formations of pits on the surface in contact with hot plastic results in reduced service life due to fatigue and erosion wear. This causes loss of productivity and hence increases production costs significantly. Therefore, improvement in the surface properties of the pre-mould steels becomes important. The service life of these components can be improved significantly by carefully modifying the microstructure of the material to give high surface hardness and a tough core. Plasma nitriding process is widely accepted by the plastic industries for providing high surface hardness and thick nitride layers.

The cavity and the core inserts are made of P20 steel. P20 steel is'nitridable steel' because the chemical composition of this steel favours the formation of stable nitrides [ASM 1995]. The plasma nitrided components gave a surface hardness of 800 HV and a case depth of 425 microns. The surface hardness of plasma nitrided P20 steel is higher compared to gas or liquid nitrided P20 steel [Ganguli 1996]. This is due to the presence of higher nitrogen incorporation by plasma nitriding on the surface. The plasma nitrided components survived more than one million operation cycles as compared to half a million shots of a non-plasma nitrided component. The life of the moulds is considered over, when flashes of the plastic material are observed at the parting surface. A thorough investigation of the parting surface revealed that it was partly eroded and showed a few numbers of pits distributed non-uniformly over the entire surface. The pit size was more than 100 microns and irregular in shape when viewed under the optical microscope. Erosion of the parting surface was caused by the impingement of the hot thermoplastic melt at high injection rates. Moreover, microcracks also formed because of the repeated stress on the parting surface during consequent shots.. Eventually these cracks coalesce, and pits are formed [Bhusan]. As a result of the non-uniformity of the surface excessive plastic get collected at the edges of the component. Hence, a combination of fatigue and erosion wear deteriorates the performance of the plastic moulds in production.

The nitrided components showed no significant dimensional changes. There was minimal distortion of the surface, which was well within the dimensional tolerance. Surface hardness values measured on the surfaces did not vary drastically i.e. average value was 768 HV, a decrease by ~32 HV. The increase in surface hardness on the eroded surface may be the result of stresses developed during plastic processing.

The case depth measured according to the definition of core hardness 50HV was calculated to be ~250 microns after use as compared to the 425 microns of the plasma nitrided component. This meant that only half of the case was used up during the trial. The moulds are still hard and could be reused after a slight grinding. This is due to the presence of nitride precipitates in the diffusion zone, which contributes to hardness without providing crack nucleation sites. Also, since, the erosion pits are not deeper than 150 microns as measured by surface roughness profilometer, the component can be utilized after minimum grinding.

Hence it can be concluded that the service life of the plasma nitrided plastic moulds increased by a factor of two as compared to the non-plasma nitrided moulds. This resulted in indirect savings in terms of reduced downtime. Moreover, moulds were not seriously damaged and could be reused after minor grinding as part of reconditioning operation.

Plasma nitriding is extensively used in plastic processing machinery. Extrusion screws and barrels made of EN-41B are nitrided to enhance the life of the components by increasing wear resistance. The hardness achieved is 70-72 RC. Components of injection moulding machines like tip, seat and valve usually made of H11 and H13 are plasma nitrided for about 16 hours. The surface hardness achieved is in the range of 70-72 RC and a case depth of 200-300 micron.

OHNS is oil hardening tool steel with low percentages of nitride forming elements. This is usually is soft annealed to about 210 HV which makes it easy to machine. A machined part is conventionally oil-hardened and tempered to have the desired hardness (570 HV to 740 HV) depending on application. Nitriding can further increase the surface hardness. On nitriding a soft annealed sample whose core hardness is about 210 HV, it is found that surface hardness has increased to 600-700 HV. However the hardness drops to 400-450 HV within 15 microns from the surface. Thereafter, the drop is slow and almost linear.

Hydropower Components

In the Himalayas, most rocks are of sedimentary type with very high silica content. This has caused most of the generating units in many hydro power stations to suffer prolonged forced outages due to damages to the under-water components on account of highly erosive action of silt in water. Various research studies have been carried out to evaluate its precise nature of effects and factors contributing to the erosion of under-water parts. Most of the hydroelectric power stations in the Himalayan range are under National Hydroelectric Power Corporation (NHPC). The monetary losses incurred by NHPC due to repairing is enormous; approximately Rs.10 million is being spent annually in replacing/ repairing worn out parts, besides the costs due to the downtime of the power station. Plasma nitriding has been tried to reduce silt impingement effects on hydropower components like sleeve drums and guide vanes [Fig. 5.10] made of AISI 13CrNi4 steel.

AISI 13CrNi4 stainless steel is a martensitic stainless steel, which is ferromagnetic and hardenable by heat treatments. It provides resistance to mild corrosion, cavitation and moderate abrasion, and they possess relatively high strength. 13CrNi4 are usually annealed at 790-815 ^{o}C. The typical ultimate tensile strength obtained is approximately 550 MPa. It is then austenized at 955-980 ^{o}C and tempered at 595-620 ^{o}C. The typical hardness is 350-400 HV. The chemical composition of AISI 13CrNi4 is given below:

The results indicated a maximum surface hardness of 1255 HV and a case depth of 250 microns on the component. The micrograph of a cross-sectioned 13CrNi4 sample showing 20 microns is shown in Fig.5.11. An X-ray Diffractogram on the treated samples revealed the presence of Fe_3N, Fe_4N and CrN phases on the surface as shown in Fig. 5.12. Since, most of the hydropower components are exposed to silt, having a hardness of 800 HV, it was believed that if the surface hardness of these components were more than 800 HV, life of these components could be increased.

Automotive Components

Carburising has been the preferred surface engineering process for various automotive components beside Chromium, Zinc and Cadmium plating for surface modification. However, Nitriding is now being increasingly used as a surface hardening technique [Huchel 1994 Remges 1990]. The freedom from distortion that accompanies plasma nitriding is one of the reasons for this change. Low carbon steels, as well as higher alloyed materials including stainless steels are currently being nitrided.

Plasma nitriding of piston rings made of SS 440B produces surface hardness more than 70-72 RC with required case depth of about 100 microns. Steering Ball Pivots made of AISI 4140 are plasma nitrided to increase wear properties of the ball. High alloy parts like the inlet and outlet engine valves made of AISI HNV3 or EV 12 are plasma nitrided with a case of 20-30 microns. Plasma nitriding is replacing chrome plating for environmental reasons and improved surface hardness. The timing gears of a diesel engine usually made of AISI 4140 is now being replaced by plasma nitrided due to the economy gained from elimination of post machining. Plasma nitriding is also chosen for differential housing and associated components because of the low distortion. The material usually chosen is low alloy steel like AISI 5135 or 5120. An 8-hour treatment gives a depth of 250 microns

Automatic gear systems, which demands wear resistance and high fatigue strength are plasma nitrided. So are synchroniser plates with internal or external toothed wheels are nitrided. Stacking together a number of plates mask the body and exposes only the teeth for nitriding. Nitriding crankshafts have become more popular lately because of the considerably higher bending and torsional fatigue obtained. The distortion is below 10 microns.

One of the most successful applications of plasma nitriding that has been reported is that of a malleable iron synchroniser hub made by a U.S. automotive producer. The conventional nitriding treatment of the hub caused a scrap rate of over 28 per cent because of the low distortion requirement on the part. The plasma nitriding method, which offers more control on the process and hence could meet the low distortion requirement, brought down the scrap rate from 28 per cent to 2 per cent.

Replacing carburising of timing gears of a diesel engine by plasma nitriding achieved a cost reduction because a number of machining and working processes were eliminated. The fatigue strength increased to (H)=1,300 N/mm^2 at the pitch and to (F)=700N/mm^2 at the root; case depths of > 300 microns and surface hardness of > 615 HV were achieved.

The differential housing and other components installed in 4-wheel-drive cars, which use the Visco-drive (using high viscosity oil) system. Plasma nitriding was chosen because of its low distortion effect and the possibility of solid masking. The materials used are low alloyed steels (i.e. AISI 5135 or 5120). The average cycle time is about 8 hours, including heating and cooling.

Machine Tools

The wear behaviour of plasma nitrided H13, D2 and L7 tool steel rolls and other components used in the steel industry has been studied recently [Uma Devi 1999.]. These are used in wire and rod mills and subjected to a complex contact modes including, impact, sliding and rolling. Adhesive and delamination wear processes contribute to the damage of the H13 steel rolls, which is significantly decreased after nitriding.

In many forging applications, several dies are required to complete a single production and die life influences both tooling cost and operating cost efficiency. Forging dies are nitrided to increase their surface hardness to reduce erosion wear. It is found that plasma nitriding of H-13 dies nearly doubled die life and improved forging efficiency. The initial core hardness of the material hot worked is RC 40, which increased to almost RC 70 and 100-500 micron case depth after nitriding.

In processing cold working tools, it is often essential that the high core strength developed in hardening and annealing is not reduced by the subsequent nitriding treatment. For this reason, low temperature plasma nitriding is adopted.

Plasma nitriding can also be successfully used for hardening the edges of cutting tools. In comparison with other hardening methods, tool plasma treatment has a number of advantages. Cutting tools are usually produced from high carbon steel and alloy steel consisting of elements like Chromium, Vanadium, Molybdenum. These tools are hardened and annealed to about 64 RC. A case depth of 20-30 micron with suppressed white layer is usual. In addition, a number of machine tool components like shafts, screws, screw heads, punches, guide trolls etc have been plasma nitrided.

Railway Components

Plasma nitriding is mainly used for treatment of the component parts of diesel and electric locomotives [Yaoxin 1978] requiring high resistance to wear and high fatigue strength.

The crankshaft is an important moving part of locomotive diesel engine. These are usually made of EN 24 and are plasma nitrided to have a case depth of 500 microns and a hardness of up to 60 RC. The nitrided case presents good quality with less brittleness with very low deformation. The gas consumption is reduced by 75 percent and energy consumption by 40 percent.

Valves are important parts of a diesel engine, working at 400-650 degrees subject to scouring and corrosion induced by high temperature gases. The valve stem is required to be resistant to heat, wear and corrosion. They are plasma nitrided to a case depth of 30-80 microns, with a hardness greater than 60 RC.

Guide rods for valve rocker arm made of EN 19B is plasma nitrided with case depth of 400-500 microns with hardness greater than 50 RC. Over speed shutdown shaft made of material similar to EN 41B is nitrided with a case depth of 300 microns and harness close to 65 RC. Similarly, components like supporting pins, forked joints, connecting bars, reversing gear of transmission box and transmission shaft are also nitrided.

Plasma Nitriding of Gears

Plasma Nitriding is an alternative that remains to be fully exploited by the gear industry although there are many advantages that ion nitriding offers to gear makers.

Grinding has become a routine part of gear making, primarily because the heat treating processes that harden load-bearing parts such as gear teeth also introduce thermal stresses that cause distortion. For any manufacturing operation, grinding adds time and labour and an element of risk. But unlike induction hardening, a commonly used surface hardening process in which gear teeth are hardened tooth by tooth plasma nitriding introduces favourable compressive stresses.

Worm and pinion shafts are also good candidates for plasma nitriding. Parts that are usually made from 8620 steel and carburized, or from medium alloy carbon steel and induction hardened need to be rough machined with extra material on the journals. This allows for finish machining overcoming the distortion resulting from carburizing or induction hardening. With plasma nitriding, this is not a requirement.

Worm gears typically made from 8620, 4615 or 1045 steel have a tendency to unravel when carburized or induction hardened, which means they have to be ground afterwards to make them straight and true with respect to the bore. It is found that nearly the same hardness could be achieved by making the gears out of pre-heat treated 4140 steel and plasma nitriding them.

Gear materials most commonly plasma nitrided are the 4000 and 5000 series medium alloy steels and occasionally, the 6000 series steels. Stainless steel, which is very hard to gas nitride without mechanical or chemical surface treatments prior to processing, can be also plasma nitrided.

The real advantage for a gear manufacturer is the reduced number of machining steps coupled with the quick turnaround, which results in higher throughput. With plasma nitriding, workpieces may have to be masked to ensure that surface hardening occurs only where it is supposed to. Sometimes this is relatively easy; i.e., gears can be stacked, permitting nitriding of the teeth with just the topmost pieces requiring a mask to cover the face and bore.

Plasma nitriding of electroplated chromium

Electroplated chromium layers of few hundred microns are used primarily to increase service life of functional parts by increasing their resistance to wear, oxidation and corrosion. Inspite of its widespread applications, there are certain limitations in its use. The hardness of electroplated chromium decreases progressively with an increase in temperature especially above about 205 C; thereby affecting the wear resistance adversely. Also, the undesirable microcracks and porosity generated during the electroplating process lowers the wear and corrosion resistance [ASM]

In order to overcome these disadvantages, the surface of electroplated C chromium is modified by means plasma nitriding [Matsuda1983 Ge1996]. The improvements in wear and corrosion resistance is attributed to the formation of hard Chromium nitride compounds like CrN and Cr_2N. The modified layers obtained by these processes were of the order of 3 microns [Menthe1999]. Higher case depth is obtained with elevated temperature. A large fraction of Chromium is converted to CrN, and a case depth of 50 microns is obtained at 1000 C, in 3 hours. Commonly used parameters and techniques for forming thick case depths with plasma nitriding of austenitic stainless steel, have been found unsuitable for processing electroplated Chromium. The results also indicate that diffusion coefficients are very similar to that of Nitrogen in Titanium.

The bulk properties of the substrate material may deteriorate with high temperature. The microhardness of the SS316LN substrate remains unchanged even after the high temperature treatment. SS316LN may, however, undergo sensitisation and loose corrosion resistance. Moreover, other mechanical properties, like toughness, ductility, tensile strength may be affected.

Plasma Nitriding as Alternative to Chrome Plating

Hard chrome plating is an electroplating process to deposit Chromium on engineering tools for wear and corrosion resistance. During electroplating large amounts of Hydrogen gas bubbles burst out throwing a mist of hexavalent Chromium into the surroundings. Hexavalent chromium is a health hazard (remember the villain in the Hollywood movie Erin Brockovich?) and the US EPA has set 0.015 mg/dscm as the emission limit and OSHA has proposed exposure limit at 0.5 µg/m^3. Plasma nitriding is increasingly replacing hard chrome plating in the automotive and plastic injection moulding die applications, which are subject to extreme wear conditions.

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Table I: Different oxidising processes

Species	**Process**
O	Oxidizing (blue) of tools
O	Oxidizing of nitrided layer
O + N	Oxinitriding
O + N + C	Oxinitrocarburizing
O + S + N	Oxisulfonitriding

Table II: Plasma Nitridable Steels

CLASS	Material SAE/En	Temp. °C	Surface Hardness (HV)	Case Depth (mm)
Carbon Steels	1040 En 8	550 - 570	500 - 700	0.3 - 0.6
Heat Treatable Steels	4137, En 19	510 - 530	500 - 700	0.3 - 0.5
	58CrV4, En47	500 - 520	600 - 700	0.3 - 0.5
	4340, En 24	530 - 550	600 - 800	0.3 - 0.5
Nitriding Steels	En 41B	520 - 540	900 - 1200	0.3 - 0.5
Hot Working Steels	H11	510 - 530	900 - 1300	0.2 - 0.3
	H13	510 - 530	900 - 1500	0.2 - 0.3
Cold Working Steels	D_2, HCHC	470 - 490	900 - 1300	0.1 - 0.15
Oil Hardening Steels	OHNS/AI SI01	530 - 550	500 - 700	0.3 - 0.6
Low Carbon Mold Steel	P 20	520 - 540	700 - 900	0.3 - 0.5
	P21	480 - 500	600 - 800	0.1 - 0.15
Ferritic& Martensitic Stainless Steel	420	520 - 540	1000 - 1300	0.05 - 0.1
	440B	560 - 580	1000 - 1300	0.15 - 0.2
	13Cr4Ni	530 - 550	900 - 1200	0.15 - 0.25
	410	540 - 550	900 - 1200	0.10 - 0.15
Austenitic Stainless Steel	304	560 - 570	1000 - 1300	0.05 - 0.10
	316	560 - 570	900 - 1200	0.05 - 0.10
	201	560 - 570	900 - 1500	0.05 - 0.10
Precipitation Hardened Steel	17-4 PH	460 - 480	1200 - 1400	0.05 - 0.10

Table III. Moulding steels and their mould life

Material	Rockwell Hardness, R_c	Mold life (cycles)
S7	59-61	1,000,000
H13	52-54	1,000,000
SS420	52	1,000,000
Moldmax-High Hardness	46-42	500,000
P20	28-32	500,000
MoldMax-Low Hardness	26-32	500,000
Ampcoloy 940	20	100,000
AL Q7	16	100,000
Al 7000	14	100,000
Al 6000	8	100,000

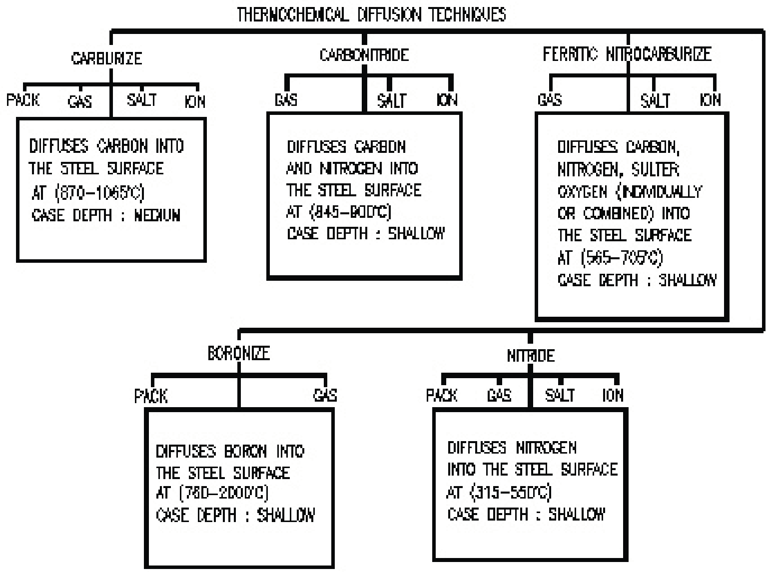


Fig. 5.1. Categories of thermochemical diffusion processes

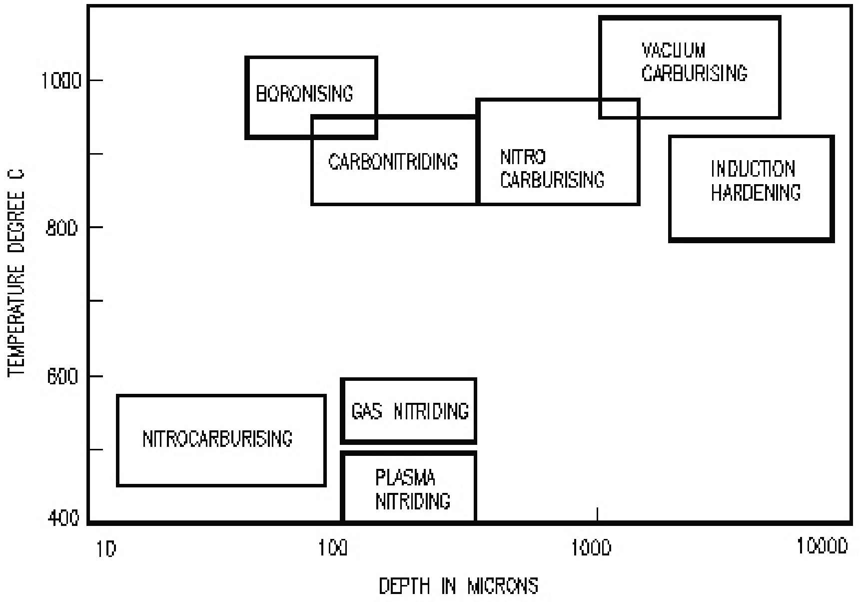


Fig. 5.2. The processing parameter space for thermochemical diffusion treatments

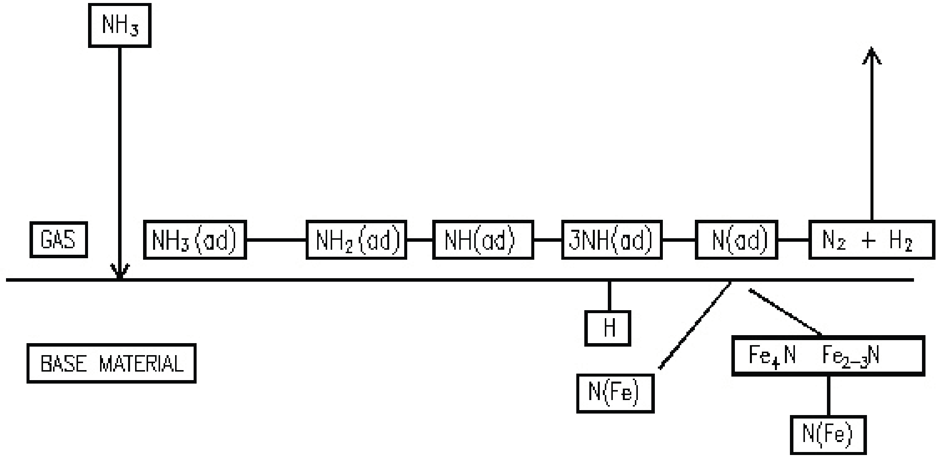


Fig. 5.3. The gas nitriding process

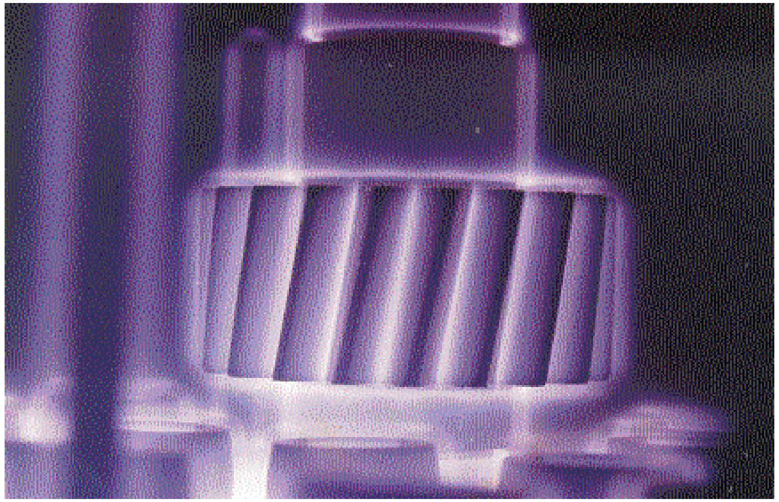


Fig. 5.4a. The plasma nitriding process: a gear immersed in nitrogen hydrogen plasma

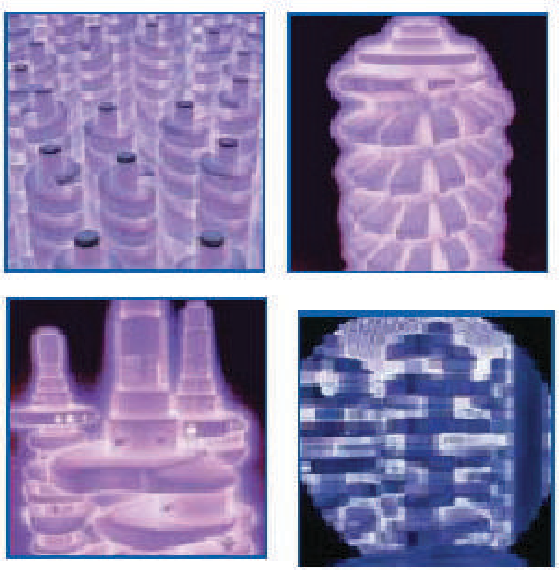
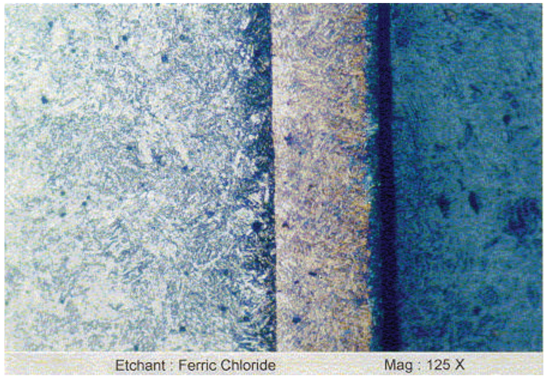


Fig. 5.4b. Stacks of work pieces being plasma nitrided (Photo courtesy Metaplas Ionon, Germany)



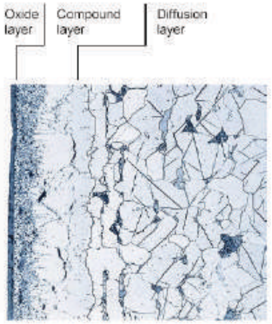


Fig. 5.5a. Different layers of a nitrided material. Fig. 5.5b. Detailed view of microstructure of IONIT treated steel (Photo courtesy Metaplas Ionon, Germany)

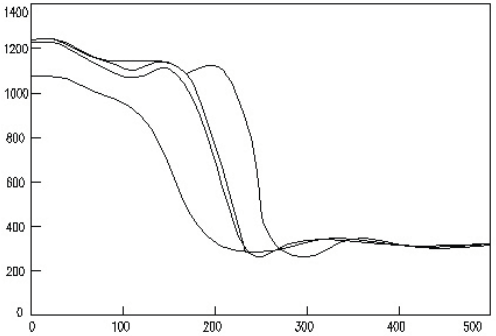


Fig. 5.6. The profile of hardness for a nitrided sample

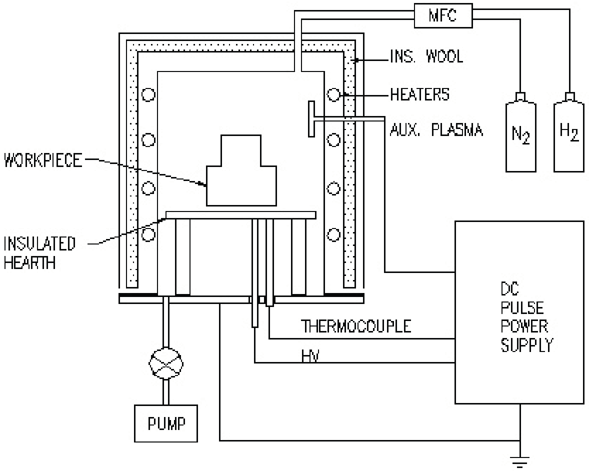
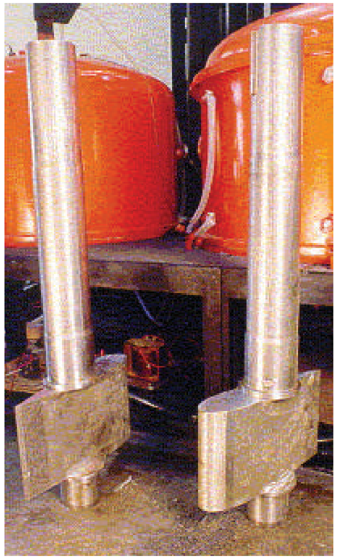


Fig. 5.7. Schematic diagram of a plasma nitriding reactor

Fig. 5.8a. Photograph of a commercial plasma nitriding system (Figure courtesy of Metaplas Ionon, Germany). Fig. 5.8b. Work pieces being stacked for nitriding (Figure courtesy of Metaplas Ionon, Germany)

Fig. 5.9. Photographs of plasma nitrided components (Figure courtesy of Metaplas Ionon, Germany)



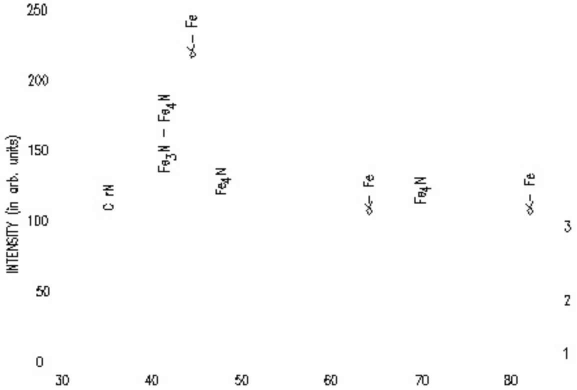


Fig. 5.10. Photograph of large guide vanes used in hydropower generation for plasma nitriding. Fig. 5.11. X-ray diffractogram showing the presence of iron nitrides in nitrided steel

6. Alchemy by Implantation

Surface Modification by Ion Implantation

Ions accelerated in plasma can be implanted into materials to modify their properties. The plasma ion implantation technique is less expensive compared to implantation using high-energy accelerators. The material properties can be changed to improve wear and corrosion resistance. Plasma implantation can also be used to assist other plasma-based coating processes. A recently developed area of application is the doping of semiconductors.

A spin-off of the nuclear physics research in the 1960's was the availability of particle accelerators capable of accelerating nuclei to very high energies. Shot into solid surfaces, these nuclei would penetrate deep inside the surface. This process is called ion implantation and the first industrial application was doping of semiconductors [Pieraux 1984]. The idea of using implantation to modify the surface properties of metals [Hartley 1975] emerged in the early 1970s. Implantation of Nitrogen, Carbon or Boron into steel results in chemical and microstructure changes at the surface with substantial improvement of the material performance due to improved resistance to corrosion, wear, fatigue etc. resulted.

When compared to conventional thermal and chemical surface engineering techniques, ion implantation has the following significant advantages [Williams1984, Rimini 1995, Hirvonen 1996, Nolfi 1983]:

- Surface properties can be selectively changed without changing bulk properties.
- The modified surface layer being integral to the material does not fail by bonding failure or delamination.
- There is no associated dimensional change since it is not a coating process.
- Changing the implantation energy can change the concentration of the implant species and the depth of penetration.
- Since implantation is a non-equilibrium process, the alloying is not limited by thermodynamic properties and diffusion kinetics.
- Since it is a cold process, there is no dimensional change due to thermal distortion and degradation of surface finish.

Despite these promising features, accelerator-based ion implantation did not catch on in industry. The reason for this becomes clear if one examines the technology in detail. An ion accelerator shown schematically in Fig. 6.1 is an expensive and sophisticated equipment. The basic equipment contains a plasma ion source maintained at high voltages, precisely machined and positioned extractor electrodes, magnetic mass separator and evacuated drift chamber. The dosage is limited by the flux of the beam and is typically in the milliampere/cm^2 range covering a small area. It is a line of sight process and hence irregular shapes are imperfectly implanted even with complex beam rastering and manipulation of the work piece. The disadvantages of beam-line processes are the high costs associated with low throughput, and the line of sight restrictions on implantable geometry. For certain applications where a non-planar target is to be implanted, target masking is essential to achieve uniform implantation.

Plasma Ion Implantation

Conrad and Castagna invented the technique of using a plasma medium to directly implant ions in 1987 [Conrad 1987]. It is based on the phenomenon that a conformal ion sheath surrounds any object immersed in plasma and is biased to potentials negative with respect to the plasma potential. Under equilibrium conditions, the ion sheath delivers an ion flux to the electrode at a rate determined by the flow of ions into the sheath from the pre-sheath at the ion acoustic speed as shown in Fig. 6.2. A similar technique was invented almost simultaneously in Australia [Tendys 1988]. The class of techniques of implantation where the object to be implanted is immersed directly in a plasma are known variously as "Plasma Ion Implantation (PII), Plasma Immersion Ion Implantation (PIII), Plasma Source Ion Implantation (PSII) or Plasma Based Ion Implantation (PBII)".

The fundamental time scales relevant to the plasma ion implantation process are schematically shown in Fig. 6.3. On application of the negative voltage pulse on an electrode immersed in uniform plasma, electrons are expelled from the region near the electrode object. This takes place in a time scale of the order of the electron plasma period, which is the inverse of the electron plasma oscillation frequency. This is typically, nanoseconds for low-density plasmas. During this time the ions do not move at all, so that as the electrons recede, they leave behind a region of nearly uniform, stationary ion space charge. This is called an ion matrix sheath and usually has a parabolic potential distribution. Various ion matrix sheath models give finer variations of the potential profile.

Over a slower, ion plasma time scale of microseconds, ions are accelerated and begin to move towards the electrode. The maximum energy they gain is the sheath potential drop. They are embedded on the electrode surface determined by the penetration depth, which is a function of the applied potential and the material density. With the ion depletion, the sheath edge expands into the plasma at a rate determined by the ion sound speed. Ultimately, an equilibrium sheath thickness determined by the balance of the ion loss and the ion replenishment into the sheath is established.

The conduction current is continuous across the sheath. This requires that the Child's law current density is equal to the charge crossing the sheath boundary in unit time [Stewart 1991]:

$$I = (2/9)\, A\, (2e/M)^{1/2}\, e\, n\, V^{1/2} / (1 + (2/3)\, w\_\{pi\}\, t)^{2/3} \quad ...1$$

In an expanding sheath the electric field changes with time and the resultant displacement current must be taken into account. This implies that we must assume the continuity of the total current rather than that of the conduction current alone. Considering the sheath as a variable capacitor with time-varying thickness [Mukherjee 1995] can provide an elegant solution.

$$I = dQ/dt = C\, dV/dt + V\, dC/dt = V\, dC/dt \qquad ...2$$

The capacitance of the sheath is greater than that of the vacuum capacitor with same parameters, because of space charge effects.

$$I = \frac{(2/9)\, A\, (2e/M)^{1/2}\, e\, n\, V^{1/2}}{(1 + (2/3)\, \square_{pi})\, t^{4/3}} \qquad ...3$$

Equation (3) indicates that in an expanding collisional plasma sheath at initial times, the current density increases as $t^{3/2}$ whereas at later times it falls as $t^{4/7}$ though the bias applied can still increase linearly at time.

On a larger time scale of the order of many ion plasma periods, the sheath reaches a steady state. The Child law now gives the current density at the electrode and the sheath thickness is approximately given by:

$$D = {}_{D}\, (eV/kT_e)^{3/4}$$

For plasma of density $10^{10}/cm^3$ and 1 eV electron temperature, the sheath thickness for a 100 kV bias is of the order of 40 cm. Here the sheath is assumed collisionless. However, there can be charge exchange collisions approximated by a constant mean free path and conserving ion flux. It is also assumed that the biased electrode is perfectly absorbing and secondary electron emission from the electrode does not take place. The presheath is not considered in the present calculations, as the potential drop in the presheath is small.

Since the sheath covers the electrode entirely, the deposition is uniform. The total flux can be many orders of magnitude higher than the accelerator process, which cuts down the time to attain the required dosage. The surface area of the work piece can be arbitrarily large.

The implantation of energetic ion into the solid is followed by a number of events. The slowing down process is shown in Fig. 6.4. The energetic ion slows down to solid-state binding energies quite rapidly (in times of the order of 10^{-14} s. The products of ion interaction with the atoms of the solid also cool in about 10^{-12} s). Radiation defects formed during these phases are partially annealed. During these phases an internal churning and mixing of the subsurface atoms occurs. At high substrate temperature, sometimes produced by the implantation process itself, thermal diffusion of the implanted atoms and of the defects occurs. These are slow events taking place in hundreds of seconds. The chemical and compositional structure of the subsurface region gets altered during these processes. The chemical reactions involve formation of new phases [Nolfi 1983], which may be homogeneous or form precipitates. All these phenomena are influenced by the presence of radiation defects.

For energetic ions, sputtering yields can be of the order of unity resulting in continuous erosion of the implanted surface. With increasing fluence, the surface erosion penetrates into the previously implanted zone. A stationary profile is established with a balance of surface erosion and implantation.

Plasma Ion Implantation is technically much simpler than accelerator-based implantation for the following reasons:

1. Elimination of the need for target manipulation and beam rastering
2. Elimination of target masking requirement
3. Ability to maintain near ground potential at the ion source hardware and control
4. Higher productivity both in continuous and batch processes
5. Ability to handle large or heavy targets with complex geometry.

Ion implantation provides a versatile and controllable means of introducing selected additives into any material for research aimed at studying their effects on material properties, and the redistribution that may occur during wear or thermal treatment. After implantation, some metals show increased resistance to wear and oxidation due to the formation of hard damaged layers on the surface of the metal. These layers resist further oxidation and thus protect the material underneath. The major advantage of ion implantation over plating techniques is that implantation does not change the size or shape of the target, yet it can significantly extend the life of machined parts and tools.

Alteration of polymers is yet another application. In most polymers, ion implantation creates a highly conductive layer near the surface with a low-conductivity layer underneath. The highly conductive layer is formed with high implant energies. Besides the formation of these layers, most implanted polymers tend to resist solvents and show increased mechanical hardness. These properties, together with the temperature sensitivity of the conduction layers, suggest several applications. Strain gauges, temperature sensitive packaging and very small size resistors have all been created with ion implanted polymers.

PII processes may be ideally suited for surface engineering of metallic and ceramic components to realise improved performances in terms of the following surface dependent properties:

1. Wear and abrasion resistance.
2. Oxidation resistance.
3. Corrosion resistance.
4. Fatigue resistance.
5. Friction/lubrication.
6. Hardness.
7. Electrical conductivity of semiconductors (metallization).

Plasma Ion Implantation Reactors

The industrial plasma ion implantation reactors [Fig. 6.5] consist of a vacuum chamber and pumping system, plasma source, high voltage pulse train generator and controls.

The size of the vacuum chamber is determined by the number of parts per batch with the assumption that these parts are mounted in a single plane at the centre of the cylindrical chamber. This plane has to be well within the sheath. A 100 kV sheath can be as thick as 40 cm and hence this puts limits on minimum sizes of implantation reactors. The sheath must be collisionless to avoid collisional scattering of accelerated ions while traversing through the sheath, which can result in energy dispersion of the implanted ions. This demands that the background gas pressure must be less than 10^{-4} torr. The vacuum pumping system consists of a booster pump, diffusion pump and a cryogenically cooled baffle for water vapour removal.

A typical high voltage pulse generator based on tetrode electron tubes switch an applied high voltage directly with the switch parallel to the load resistance [Fig. 6.6]. When the tetrode is non-conducting, the capacitor C will be charged by means of load resistance R and plasma. When the tetrode is switched <NOBR></NOBR> a negative voltage pulse appears on the workpiece. This type of switching has the advantage that the filament and grid control is near ground level. The form of the pulse is variable within wide limits and depends very little on the load resistance. The typical duty cycle is a few percent, but can be increased up to 50 per cent if a fast capacitor-charging device is used.

The maximum tube current and the stray capacitance determine the rise time of the pulse, whereas the stray capacitance, the charging resistor and the plasma load determine the fall time. In case of a short circuit in the load (e.g. arcing in the plasma), the cathode saturation current of the tube limits the current. The tube anode in this case absorbs the full pulse power. All tubes can stand off such short circuit operation within certain limits.

The pulse capacitor C is sized (10-1000 nF) such that the current for the whole pulse will produce a droop in voltage of <10 per cent. The choice of the loading resistor depends on the requirements of the form of the pulse, duty cycle, frequency, and voltage. The smallest possible resistance is found by considering that during a pulse no more than <NOBR>10-20 per cent</NOBR> of the maximum tube current should flow through the loading resistor. A small loading resistor also leads to short turn-off times with typical values at <NOBR>3-300 k□.</NOBR>

The switch is the most expensive component and is usually a tetrode capable of holding the required voltage and current. Gridded tubes are available from Eimac, Brown Boveri and Thomson CSF with voltage and current capability upto 200 kV 250 A. Beam switch tubes have a magnetron geometry and are available upto 175 kV, 100 A. Thyratron and other gaseous switching tubes are not reliable above 70 kV.

Pulse generators based on semiconductor switches are more compact and use less power. Semiconductors, however, are sensitive to short circuits in the load and cannot be recommended for very high voltages and power. It switches the high voltage directly, i.e. with the switch in series with the load. The advantage of switching directly is that the pulse shape is variable in a wide range and that the pulse shape depends only little on the load. The circuit with the switch in series with the load has the advantage that duty cycle from <NOBR>0-100 per cent</NOBR> can be chosen.

Another expensive and demanding component is the plasma source with capability to generate large volume, medium density, and unmagnetized plasmas with low gradients in density and temperature. Inductive coupled plasma and Electron Cyclotron Resonance sources are popular. The size of the plasma region must be larger than the sheath dimensions to avoid depletion of the plasma during implantation.

The world's largest PSII Facility has been built in a collaborative programme involving Los Alamos, General Motors, and the University of Wisconsin [Mantese 1996]. The facility is a 1.5-m-diam by 4.6-m-long vacuum chamber with a high-voltage switching system capable of 60-A, 120-kV pulses with an average current of 2.4 A. It is being used to develop and verify PSII-based processes for use in extending the life of automotive components, industrial tools, and dies. Nitrogen implantation has been performed on objects with surface areas as large as 4.6 square meters.

Tribological Applications

Technological superiority of ion implantation in tribology has been recognised since long [Hirvonen 1989, Mikkelsen 1992]. However, it has to compete with plasma nitriding, which is the traditional and preferred medium-temperature diffusion process for enhancement of tribological performance of conventional tool steels. The investment and production costs of PIII being higher compared to plasma nitriding, the technique will find it difficult to compete with plasma nitriding. Capital cost is increased due to the necessity for high vacuum pumping systems to generate the considerably lower working pressure; larger volume of the vacuum system to accommodate the expanding sheath and an expensive high voltage modulator.

The higher ion energies used in implantation has significant technological advantages. For example, energetic Nitrogen ions can penetrate through the diffusion barrier formed by a surface oxides; thereby enhancing the efficiency of the nitriding process with higher Nitrogen incorporation achieved within shorter times. In materials for which only a certain maximum temperature is allowed, e.g. in order to avoid the formation of undesired phases, PIII nitriding might therefore be advantageous as the processing times can be held within tolerable limits even at large depths of nitriding.

The austenitic and austenitic-ferritic stainless steels are speculated to benefit from the PII treatment [Zhang 1985, Menthe 1995, Collins 1995, Blawert 1998]. Their high chemical inertness yields a wide range of applications. However, they have poor surface properties such as low hardness and a high wear rate. Conventional nitriding demands elevated temperatures, which transform chromium oxide into chromium nitride at the surface, resulting in deterioration of anticorrosive properties. With implantation, the surface is undisturbed retaining the chromium oxide. It is also possible to produce single-phase layers called an expanded austenite or S-phase [Samandi 1993] on these types of steels, which appear to be a solid solution of Nitrogen in an austenitic lattice without precipitation of CrN. The Nitrogen atoms become trapped at the Chromium alloy atoms with a corresponding maximum atomic concentration of about 20 per cent resulting in a lattice expansion of 7 per cent identified by X-ray diffraction. While this phase can also be obtained by plasma nitriding, PII seem to be more efficient in its formation. Compared to the untreated surfaces, the wear rates are drastically reduced, by about a factor of three in case of the stainless steel. Simultaneously, the corrosion behaviour is unaffected or even slightly improved.

PII treatment incorporating 5-6 per cent Nitrogen gives high Chromium content steels a remarkable improvement in hardness. Other strong nitride forming elements like Molybdenum and Vanadium can also achieve the same result. For steels with more percentage of Chromium it is observed that the same dosage of Nitrogen yields better hardness. Formation of chromium nitride is held responsible for this effect.

One of the very standard applications is implanting Nitrogen ions on AISI grade tool steels. The surface hardness is seen to improve by 75 - 100 per cent. In industrial field tests of Nitrogen ion implanted AISI A2 tool steel score dies used for punching Aluminium it was noted that the number of shots before die failure, increased from 8.5 to 14 million [Shamim 1994]. The number of bolts that could be effectively processed by M2 tool steel dies used for producing structural steel bolts increased from 25000 to 100000 [Conrad 1988].

PSII may be a useful surface engineering technique for components manufactured from super alloys for high temperature resistant applications. Sequential and cyclic implantation of Nitrogen and Titanium on GCr15 steel [Chan 1992)] up to a depth of 10 μm results in the increase of hardness by 42.3 per cent. Tribological properties of Inconel 718 [Mahboubi 1996] implanted with Nitrogen through PSII are significantly improved. PIII studies on tools steels produce significant improvement in wear resistance especially for high temperature implantation. PIII [Mukherjee] may yield a better surface hardening than that by RF plasma nitriding in micro alloyed steels.

Recently, PIII experiments for the incorporation of Nitrogen in material surfaces have been performed at lower substrate bias (~ - 1 kV), at high repetition rates of pulse voltages [Davis 1963]. For many applications, the resulting ion energy is sufficient to penetrate the material surface, so that the Nitrogen diffuses inside owing to elevated substrate temperature [MRS 1992, Sridharan 1991]. A wide variety of materials are reported to be treated in this way. Processing at lower substrate bias is advantageous because of reduced sheath thickness and the lower secondary electron emission yield. In addition, the low-voltage pulse equipment is considerably cheaper.

Titanium and Aluminium

PSII is also performed on non-ferrous metals like Ti. Experiments done at 20 kV, 400 C, for 30 minutes, show the formation of TiN. However, the treated layer is very thin (500 A) so the increase in hardness is also less (increase by 10 per cent). Nitrogen diffusion in Ti typically starts at 800 C, which helps in the production of TiN of thickness of few m. Ti-alloys [Samandi] can achieve a remarkable improvement in the surface dependent mechanical/electrochemical properties. Also, it is seen that Nitrogen implantation of orthopaedic alloy Ti-6Al-V and Ti-6Al-4V [Abuzriba 1993] results in significant surface strengthening. In any case, PSII has been successful in enhancing the wear and frictional properties of both the substrates.

Aluminium is being widely used in the automobile and textile industry because of the obvious advantages of its lightweight and easy machinability. Engineering applications of Aluminium are often limited by its low hardness, strength and low wear resistance. Hence there is a requirement of a surface treatment for making the surface of Aluminium hard and wear resistant. Conventional techniques of surface hardening usually adopted for steel cannot be used for aluminium because of its low melting point.

Nitrogen ion implantation not only increases its hardness and strength but also at the same time retains its property of being lightweight. For instance, treatment of Al (1050A) with Oxygen and Nitrogen plasmas [Gunzel 1994] has demonstrated that the presence of Oxygen in the steady state plasma may lead to the formation of Al_2O_3 and also reduce the hardness. However, dynamic hardness may increase by a factor of 1.2 following Nitrogen implantation. Zhang et al. [Zhang 1995] have shown that the Nitrogen implanted 6061Al may significantly improve the pitting resistance and corrosion protection of Al. Nitrogen implanted 70753 (Al-Cu-Mg-Zn) shows a decrease in wear rate by ten times in comparison to the unimplanted case. Implantation of Nitrogen in other forms of Aluminium, namely, antirust Aluminium (LF12) and industrially pure Aluminium (L2), shows remarkable increase in hardness. Oxygen implantation of Aluminium has also shown to increase the surface hardness by a factor of 1.4 times.

Diamond like Carbon

Diamond-like Carbon (DLC) has carbon atoms arranged in a diamond-like structure due to which the mechanical properties are similar to those of diamond. Recently, ion implantation using hydrocarbon gases has been applied to produce large-area, hard hydrogenated carbon (DLC) coatings on embossing dies. Pulsed DC at a few kV is employed simultaneously for plasma production and ion implantation. By the treatment, the lifetime of the dies is improved by a factor of 4-5 compared to the uncoated material. The DLC coating also avoids adhesive wear, which would degrade the pattern on the die.

DLC coatings can also enhance the surface properties of aluminium. Plasma Source Ion Implantation (PSII) is used as an intermediate process to modify the properties of the transition layer between the DLC coating and the aluminium substrate and to increase the adhesion of the coating to aluminium. Because the entire processing is done in a low-pressure plasma environment and in the same experimental device, better coating uniformity and quality is assured. As the coating is an inbuilt layer within the surface of Aluminum, finish machining and grinding is eliminated and hence the process can be used on a finished product.

Biomedical Applications

Improving the biocompatibility of materials using ion implantation alone or in combination with other PVD or CVD processes is another successful application. Titanium-based biomaterial, which has been treated using Oxygen PIII [Yang 2001] shows no significant thrombus whereas the standard low-temperature isotropic pyrolytic (LTI) Carbon exhibits a strong aggregation of a thrombus after in-vivo exposure. The bombardment with oxygen ions is used to control the growth of the oxide phases, so as to form the rutile phase. Also the biocompatibility of LTI Carbon materials profits significantly from PIII [Mändl 2001]. Due to Nitrogen implantation, the platelet density after blood exposure is strongly reduced. This is probably due to the formation of a CN_x surface layer. So far, these very promising results have not been transferred to routine surgery, which is due to a number of impeding factors, such as the lengthy test procedures, which are required legally before new artificial materials can be introduced into a human body.

PII technique can also be used successfully to implant ions on non-metallic targets. Conventional ion implantation has a problem of charging of the non-metallic material during ion implantation. The charging limits the dosage as ions are repelled from the surface electrostatically. As PII is done in a plasma environment, the plasma electrons carry out charge neutralisation automatically.

Semiconductor Doping

Controlled introduction of doping species into Silicon is essential to form active devices. Conventional beam-line implantation is used for junction fabrication in semiconductor devices. With the continuous miniaturisation leading to shrinking lateral and normal dimensions dictated by the so-called ‘roadmap’, deposition depth will correspondingly decrease leading to the demand for ultra-shallow junctions. Beam-line ion implantation fails at low energy because of the inefficiency of ion beam extraction and transport at low voltages. PIII provides an alternate doping technology for production of shallow junctions so that this technique has entered the research laboratories of large producers of ion implantation equipment for microelectronics [Felch 1998]. For accelerating voltages of 2-5 kV, an implantation depth of less than 100 nanometer is achievable. Contrary to beam-line ion implantation, the entire wafer is implanted simultaneously. The implantation time is independent of the wafer dimension and hence cost does not go up with wafer size.

The formation of ultra-shallow pn junctions by PIII has been successfully demonstrated [Jones 1996]. PIII systems have high throughput with dose rate typically exceeding 10^{15} ions/cm^2 per second. Commercial PIII systems equipped with a fully automatic load lock and wafer transfer chamber for automated wafer sequence operations are now available for implanting up to 12-inch wafers. Plasma doping is envisaged to be the alternative technique suited for the shift to simpler, more economical, higher throughput, low machine cost and room temperature operation. This technique is also compatible with CMOS production environment and cluster-compatible hardware. The technology has gained considerable momentum in the past several years and an international plasma doping users’ group has been formed to bring together equipment manufacturers, process engineers, and researchers.

PD can be implemented in three different configurations: gas source PD, solid source PD (SPD), and RVD with plasma pre-treatment. SPD is gaining popularity as the use of toxic dopant gases can be eliminated. Gas source PD is usually performed in B_2H_6 plasma diluted by He sustained by an electron cyclotron (ECR) or radio frequency (RF) plasma source. The aim of dilution is to control the implantation rate and toxic dopant species. The wafer is attached to a sample holder or chuck acting as the cathode.

Plasma doping has a long way to go before it can match the theoretical predictability of beam-line techniques. The junction depth is primarily determined by the pulse voltage and has been shown to vary linearly with this voltage over a range from 0.14-5 kV. However, in PD, all ionised species in the plasma are implanted. For example, with BF_3 gas, the predominant ions implanted are BF_2+, B+, and F+. Furthermore, the energy spectrum of the ions contains components lower than the pulse voltage due to ions present in the sheath at the onset and turn off of the pulse, as well as because of the finite rise and fall times of the pulse. While low-energy ions are not detrimental (even preferred) in shallow junction formation, both of these factors can affect the dopant depth profile. They offer the process engineer new opportunities for tailoring this profile, being of particular use for shallow junctions.

With decreasing feature size, it becomes also necessary to screen the near-surface layer of the wafer, which carries the microelectronic structures, against the underlying bulk, both in order to avoid electrical field penetration and to block diffusing impurities. For this purpose, buried SiO_2 layers can be employed. These are conventionally produced by high-dose ion implantation of Oxygen into the Silicon wafer and subsequent thermal annealing (the so-called SIMOX structure: Separation by Implanted OXygen). A well-established buried layer with sharp and smooth interfaces is obtained after annealing.

In SIMOX structures, the quality of the top crystalline Silicon layer is reduced due to irradiation defects, which remain even during the annealing at very high temperature. In order to overcome this problem, an alternative process has been proposed which is called "Smart Cut". The silicon wafer is first oxidized thermally. It is then bombarded by light ions (Hydrogen or Helium), which cause very little damage. At a sufficiently high dose, gas-filled cavities form in a shallow band close to the mean projected range of the ions. The structure is then attached with its oxidized surface to another wafer using the conventional technique of anodic bonding. With a proper thermal treatment, the bonded two-wafer structure then cracks along the plane containing the bubbles. A final surface lapping finishes the process. It has been demonstrated that buried oxide layers of a thickness of about 30 nm can be formed under a crystalline Silicon layer of about the same thickness, when the "smart cut" is induced by PIII using 35 keV Helium ions.

In a recent experiment the modification of oxidation behaviour of Nitrogen and Argon implanted Si wafers is reported. Nitrogen and Argon ions are implanted in Si at various energies at different implantation dose. Post implantation wet oxidation results show that Argon implanted Si has higher oxide layer thickness with increase in the implanted ion dose. The results can be used to control the gate oxide layer thickness for memory and logic transistors.

The growth of carbide, nitride and oxide of Silicon either simultaneously or as multilayers is also gaining increasing importance. This combines the SiC semiconductor, which is widely used in high temperature, high frequency and high power electronics, with the insulators Si_3N_4 and SiO_2, which are also necessary for semiconductor design. SiC thin films can be grown by using Methane PIII into Si at 850 ^{0}C and subsequently annealed at 1250 ^{0}C for 5 hrs. As implanted, amorphous regions are observed surrounding small heteroepitaxial grains of SiC. After annealing, the SiC is completely cubic and heteroepitaxial with a 5:4 coincidence lattice at the interface, which minimises stress due to the 20 per cent lattice misfit between Si and c-SiC. SiO_2 is grown by oxidation and stays amorphous even after the high-temperature annealing.

Plasma Ion Implantation at Elevated Temperature

Plasma ion implantation assures dose uniformity for samples of complex shapes and has higher Nitrogen incorporation rate in comparison with plasma nitriding. However, the penetration depths are determined by the kinetic energy of the ions and hence are less (10A/keV for N on Fe). For higher depths, either the kinetic energy has to be increased, or the implanted ions have to undergo diffusion inside the sample.

The hybrid process of shallow implantation and diffusion hardening (SIDH) [Mukherjee 1997 1998] takes the advantage of dosage uniformity from plasma based ion implantation and subsequent thermally enhanced diffusion of implanted ions inside the steel. Hence, this process leads to larger effective implantation depths and shorter processing times. This process is particularly suited to stainless steels, which are otherwise difficult to nitride. This process can work in a much lower temperature range than plasma nitriding and hence the chromium of the steel remains unaffected during SIDH. As a result of this the work piece retains its corrosion resistance property. Also, this lower temperature causes lower distortion of the work piece, which has been demonstrated on high precession cutting tools.

In SIDH, the samples immersed in Nitrogen plasma, are typically pulsed biased to 1 kV. This enables penetration depths of 10A, which is generally thicker than the top oxide layer present in most samples. At high repetition rates, and with significant electron collection during positive bias, the sample temperature rises. The temperature achieved is 400 - 500^o C which is controllable by varying the on and off time ratio. To achieve higher temperatures, an external heater is switched on and this allows treatment to be done at temperatures of 800^o C.

The SIDH process may have some advantages of over low temperature ion implantation or plasma nitriding. If the implanted atom can diffuse inside the material (like Nitrogen in steels), then it is necessary only to implant the material to depths larger the top oxide layer. The remaining depth can be penetrated by diffusion. SIDH exploits this, and hence can work in a much lower energy range than ion implantation. As the ion energies are less, the secondary electron emission from the sample surface and subsequent X-ray generation is minimal. Also, in SIDH as the plasma production is independent of the sample bias, the plasma densities can be made to be high, and hence the ion flux to the sample can be controlled separately.

Micro hardness of AISI 5200 steel has been increased by a factor of 3 to 4 with a case depth of 40 micron by this technique [Rao 2002] using 1 kV pulses. The hardness increase is attributed to solid solution and precipitation/dispersion hardening due to the finely distributed Fe_xN nitrides. These nitrides have been identified as $Fe_{2-4}N$ by XRD and XPS analysis. Austenitic and austenitic-ferritic stainless steels treated by Nitrogen implantation appear to produce solid solution of Nitrogen in an austenitic lattice without precipitation of CrN. This phase is called expanded austenite because of the shift in the diffraction peaks. Ferritic structures in these steels completely transform into austenitic structure. It appears that ion implantation is more efficient than plasma nitriding in producing this transformation [Mordike 1998]

Industrial Status

Despite the conceptual simplicity, ion implantation is complicated in practice. Ion collision cascades, being non-linear processes, are very sensitive to initial conditions. There are several parameters to each implant that must be carefully controlled to ensure consistent, reproducible implants. Fortunately, ion implantation affords us this level of control. Material modification by ion implantation can be expensive at times. Several factors influence the cost. As mentioned before, ion implanters are complicated and expensive machines and this cost is passed on to the consumer. Ion implanters also require regular maintenance and cleaning as well as constant supervision. This adds still more to the cost. The cost is also affected by the implantation itself. The time of the implantation is also increased for higher fluences.

Finally, the difficulty of the implantation is a factor. Processes that require complex masks and multiple species of implant ions will be more expensive than single-species implants.

Large volume plasma sources and high power pulsers (100 kV, 1000 A) are the critical components which, being non-standard, determine the capital cost of ion implantation systems. Another disadvantage of plasma ion implantation, when compared to beam line implantation, is the absence of mass separation. Hydrogenated compounds of the elements to be implanted, for example NH_3 for Nitrogen, can obviate this problem. Using mixtures of compounds, controlled multispecies implantation at a single step may be possible [Le Couer 2000]

As a further advantage of PIII, it can be combined with the deposition of thin films similar to ion-beam assisted deposition. With respect to its vacuum conditions, it is compatible with physical vapour deposition (PVD) such as evaporation or magnetron sputtering. Like ion beams for IBAD, PIII may be added using non-reactive or reactive gases, enabling the formation of compound films in the latter case. Other combinations are possible with plasma processing such as plasma etching or plasma-enhanced chemical vapour deposition.

At present, plasma ion implantation techniques have not yet been established in broad fields of industrial production although several applications appear to be very promising. For the transfer from scientific research and laboratory development to industrial application, the feasibility is critically determined by aspects such as safety, duty time of the device, up-scaling and the possibility of large-area processing, and in particular the processing costs. PBII has to compete with a number of techniques, which are well established and have been developed through many years, such as plasma nitriding for tribological purposes or conventional ion implantation in microelectronics. Therefore, it has to be clearly demonstrated that PBII allows to realize new and improved surface properties at no or tolerable increase of the production cost.

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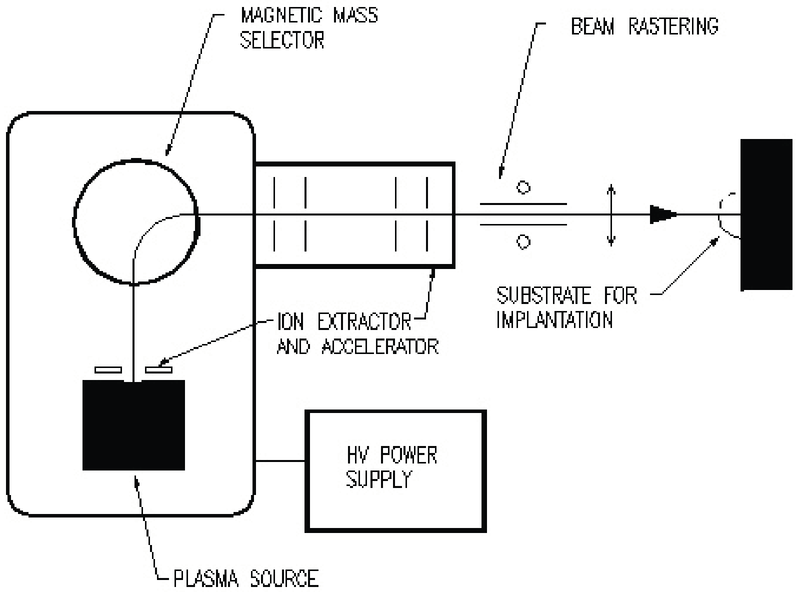

Fig. 6.1. Particle accelerator for ion implantation

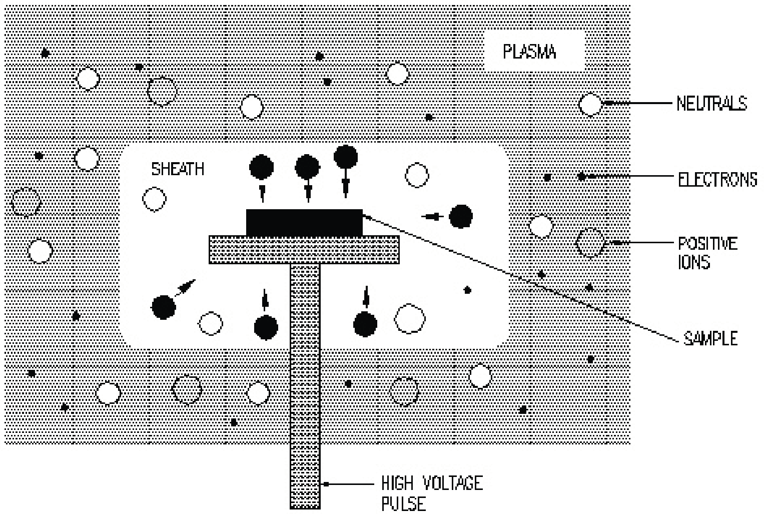

Fig. 6.2. The plasma sheath in plasma ion implantation replaces the complex optics of a conventional accelerator

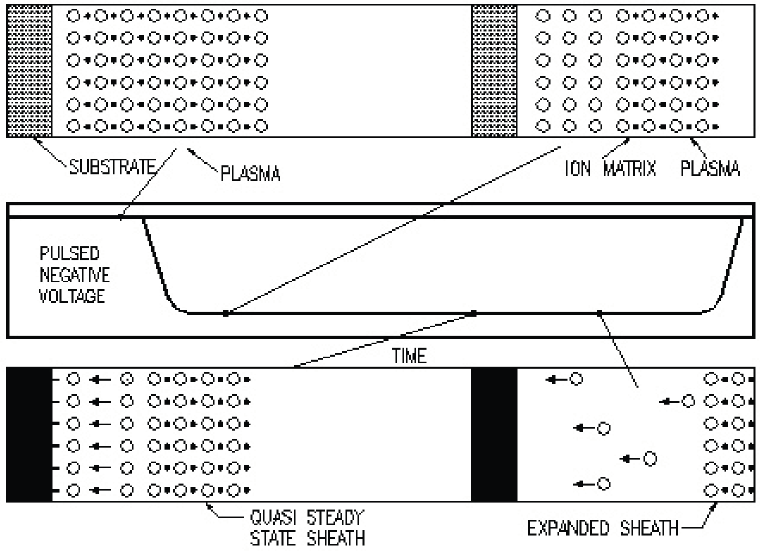

Fig. 6.3. Fundamental time scales in the plasma ion implantation process; The formation of the ion matrix sheath and its collapse

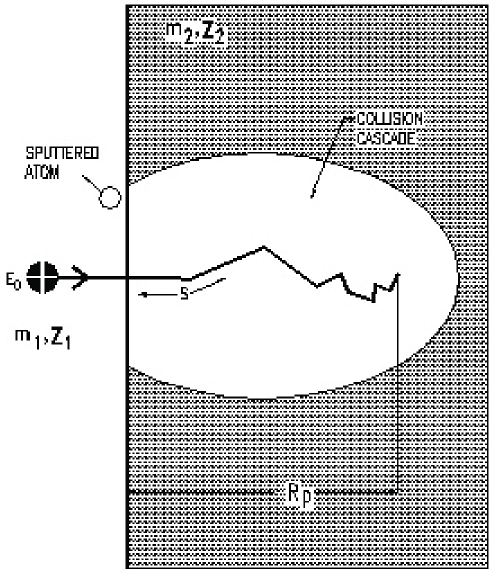

Fig. 6.4. The energy loss processes for an ion implanted into a solid

Fig. 6.5. Photograph of a commercial plasma ion implanter with the power supply and the implantation reactor

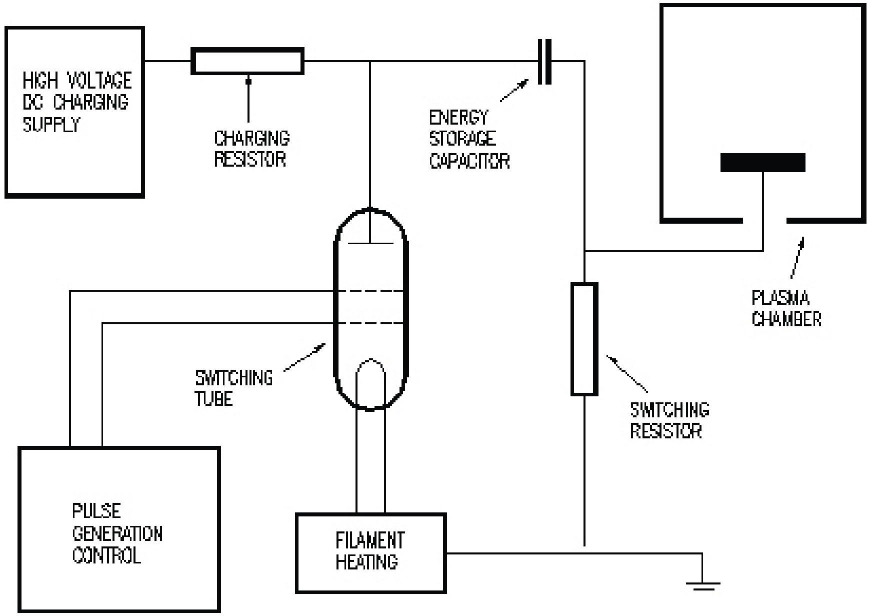

Fig. 6.6. Pulse generation technique for ion implantation

7. Engineering the Tools

Surface Engineering by Functional Coatings

Wear of engineering tools and the friction caused by bad tools has both direct and indirect impact on manufacturing cost. Depositing hard coatings on the surface can decrease wear and increase tool life and performance. This chapter discusses various methods of plasma-based deposition of advanced coatings on engineering tools and describes the properties of coated products.

Surface Engineering

Wear limits the life of mechanical systems. Wear is cumulative and can be non-linear, as worn out parts increase the wear of other parts. Wear of engineering tools and the friction caused by bad tools has both direct and indirect impact on the cost of manufacturing. Direct cost incurs in tool replacement and energy utilisation while the indirect cost is in repair, productivity loss due to downtime or breakdown of secondary machines. Data from VDI Technology Centre in Germany suggests that direct cost due to wear is DM 40 billion in Germany alone [Friedrich1998]. The US economy, on the other hand, suffers an estimated annual loss of almost $ 100 billion due to wear [Peterson 1980]. The wear-free haven of engineers is thus a goal driven by economic and productivity concerns. This goal is being approached through many technological advances which aim at longer lasting parts, zero-wear parts, and finally self-repair. Since the estimated world-wide market for cutting tools is of the order of $10-12 billion, these concerns have strong commercial basis.

Wear is the surface damage that occurs when contacting materials move with respect to each other [Goode 1989]. Even smooth polished surfaces have direct contact at many protruding points called asperities, which are subject to very high loads. During the course of relative sliding, local welding and destruction occurs at the contacting asperities, which result in the formation of hard composite particles. These particles are abrasive and remove material from the parent surface resulting wear and material loss.

The productivity in machining depends on the cutting speed and feed rate. In the conventional machining, abrasive wear is important. In high speed machining, the heat generated in the tool produces high temperature dissolution of the tool material. This chemical wear eventually leads to cratering and failure. Increased feed rates induce higher induces higher mechanical stresses on the tool, which causes plastic deformation, chipping or fracture of the tool edge.

An ideal tool should possess high hardness, fracture toughness and abrasive wear resistance. Machining operations such as milling, and the finishing of irregular parts and components such as castings produce high thermal stresses. The tool material should possess high thermal shock resistance, and in many cases, a high deformation resistance. Cutting operation produces high temperatures and the material of the workpiece reacts thermo-chemically with the tool, causing chemical erosion of the tool due to the dissolution of the tool material in the work-piece. High chemical stability is thus a necessary property of the tool material. High transverse rupture strength is also a critical requirement.

The hardness of a material is related to its bulk modulus B, which is influenced microscopically by defects, dislocations, structure of grain boundaries in nano or poly-crystalline materials, crystallite size and porosity. The bulk modulus of an ideal crystal depends on bond length d, nature of the chemical bonding and the crystal structure. It can be expressed by a scaling relationship empirically developed by Cohen [1985] as:

$$B = N_e\ 197I-220\ \square\square/\ 4\ d^{3.5}$$

Here N_e is the average co-ordination number, d is the bond length in A and I is the parameter describing the iconicity of the chemical bonding. Solids with small covalent bonds exhibit the highest bulk modulus. Diamond has the smallest bond length 1.54 A

A single material does not possess all these properties simultaneously. Most steels and non-ferrous materials such as Aluminium alloys are relatively easy to machine in contrast with stainless steels, heat-treated steels and cast irons, Titanium alloys and superalloys. Adequate performance of a given tool material thus depends on the material being machined unless the desired properties are engineered by some method. The technique of modifying surface properties to meet all the functional requirements has led to the development of a discipline called surface engineering. Surface engineering can be formally defined [Cotell 1994] as a treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material. Surface engineering involves the application of traditional and innovative surface modification technologies to engineering components and materials in order to produce a composite material with properties unattainable in either the base or surface material. For example, the substrate material can be designed to provide strength and toughness while the coating can be made resistant to wear, thermal stress or corrosion.

Surface engineering [Kumar 1999] involves techniques of surface treatment where the composition, structure or the mechanical properties of the surface are modified, or depositing a different material creates a new surface. This is essential in the application and exploitation of high performance engineering components and to counteract the rising costs of advanced performance structural materials and the increasingly high life-cycle costs associated with high performance systems. Frequently, the various surface technologies are applied to existing designs of engineering components. Ideally, however, surface engineering involves the design of the component with prior knowledge of the surface treatment to be employed.

The performance enhancement may be in engineering properties like hardness, wear and corrosion resistance or aesthetic finish, colour etc. Thin films deposited for these applications must satisfy a number of constraints depending on the final product. These include thickness uniformity, controlled stoichiometry, adhesion to the substrate, microstructure, controlled stress, stability of the coating in the operating environment, reproducibility of the coating process etc. By employing multiple coatings, interphase areas can be constructed which provide high adhesion and stress dissipation.

The requirements, which determine the choice of appropriate surface modification technique, can be either related to the substrate or to the coating. Size, shape, electrical conductivity, temperature sensitivity, and chemical composition of the surface influence the type of modification technique that can be used. Composition tolerance, uniformity requirements, coverage, deposition rate, thickness precision, and freedom from impurities and defects are the relevant coating-related issues. The failure modes of cutting tools can be understood by examining the factors, which contribute to the performance of the cutting tool as a system. The factors include substrate, coating, tool geometry, cutting parameters, work-piece material and lubrication.

Every tool and workpiece material combination has its own safe zone of operation in which the tool life can be predicted with reasonable accuracy. Hard coatings applied to the tools enlarge the safe zone [Wijngaard J]. Low coefficients of friction and a low tendency of adhesion of the coating to the work material results in less heat generation. The low thermal conductivity of the coating produces a thermal barrier on the tool surface restraining heat transfer to the tool.

The application of hard, wear resistant coating on cutting tools began in mid-1960s, and today nearly 70 per cent of cutting tools are coated [Bunshah 1972 Mattox 1964]. Thus, coatings have become an integral part of modem cutting tool materials demanding considerable research and development effort on new coating techniques and materials for improved cutting tools.

The earliest methods used for imparting increased surface hardness and wear resistance to cutting tools involved heat treatments, such as carburizing and nitriding, when the tools were essentially made of carbon steels and high speed steels. In mid-1960s, chemical vapour deposition was used for the first time to deposit thin coatings of hard, refractory compounds like titanium carbide and titanium nitride on cemented carbide cutting tools to provide increased hardness, chemical stability and wear resistance. The physical vapour deposition techniques at lower operating temperatures capable of coating high-speed steels, were commercially introduced in the late 1970s and early 1980s, and now enjoy an almost equal status with the CVD techniques. <DIV align=left>A number of plasma assisted coating techniques have emerged and matured in the past few years [Rickerby 1991, Bhat 1989, Kumar 1998, Glocker 1998, Bhushan 1991, Conference on Global Trends 1996)]. The dominant coating technique relevant to the surface engineering of engineering tools is physical vapour deposition and its variants such as reactive deposition and ion plating. Plasma enhanced CVD coating is a late entrant and is yet to be industrially established.

PVD Processes and Reactors

PVD encompasses several deposition processes in which atoms are removed by physical means from a source and deposited on a substrate. Evaporation of the target material through intense localised heating and sputtering by ion bombardment are the methods used to convert the source material into atoms. Evaporation can be by electron beams or vacuum arcs, while sputtering uses energetic ions drawn from a plasma discharge. Typically, PVD processes are used to deposit films with thickness in the range of a few nanometers to thousands of nanometers. The role of the plasma is to convert the columnar, low density coatings obtained in conventional thin film deposition into coatings with desired functional properties by modifying the film properties through ion-imparted kinetic and chemical effects [Martin 1990]. PVD techniques can also be used to form multilayer coatings, thick deposits and freestanding structures. Driven by the environmental concerns, they are also emerging as an environmentally cleaner technology when compared to electroplating and electroless processes

[Navinsek 1999]. Fig. 7.1 shows a group of commonly used PVD techniques and their parameter range.

The simplest physical vapour deposition processes are based on the fact that material vaporised from an element, alloy or compound condenses and forms a film on a substrate. A novel variation on this process involves the introduction of a gas such as Oxygen or Nitrogen into the chamber to form oxide or nitride deposits, respectively. In the reactive PVD process, a vapour of the coating material is generated from a solid target and transported to a substrate and deposited under reactive conditions. These reactive deposition processes are used to deposit films of material such as titanium nitride, silicon dioxide, and aluminium oxide.

Besides, the modern PVD process sometimes uses energetic ion beams to create dense, well-adhered coatings. This variant is called Ion Beam Assisted Deposition (IBAD) or Ion Plating.

Electron Beam Deposition

Electron beam evaporation method provides the maximum rates of deposition of metallic coatings. Evaporated atoms are in relatively low energy state (0.2 to 0.6 eV) due to which the deposited films are not very adherent or dense. The coating microstructure is highly columnar, rough and porous. Deposition of a uniform coating may require complex movement of the substrate since the vapour flux is localised and directional. Despite this, beam evaporation is probably the most widely used PVD process. High voltage electron beam evaporation is efficient but has the disadvantage of low ionisation of the vapour because of the small ionisation cross section of the energetic beam. On the other hand, the low voltage electron beam evaporation is very effective in ionising the vapour [Hakansson 1991]. Estimates put the ionisation percentage as high as 50 per cent. In addition, a large fraction of the reactive gas is also ionised.

The application of lasers to evaporate materials is an emerging area of research. Some of the main benefits are that it can be used in pulse mode to ensure congruent evaporation from alloy sources, needs no differential pumping and can be directed and scanned in a controlled manner.

The schematic diagram of a typical industrial scale PVD system [Pulker, 1992] based on low energy electron beam evaporation is shown in Fig. 7.2. The cathode of a non-self-sustaining arc discharge is a resistance heated refractory metal filament mounted in a separate chamber and maintained at high noble gas pressure. A small aperture between the cathode and plating chambers confines the arc plasma. The arc can be transferred to different anodes in the plating chamber. With sufficient power density, materials like Titanium will be evaporated and partially ionised. A negative dc bias is applied to achieve bombardment by ions of the coating material, reactive gas ions and working gas ions. The substrate ion flux determines the film deposition rate with the typical coating rate at 50 nm/min.

Balzers of Liechtenstein are acknowledged worldwide for producing high quality PVD coating using their low voltage electron beam technology [Fig. 7.3]. They have perfected high quality and highly reproducible TiN and TiCN coating technology with the additional option of CrN coating. Their technology would seem to have limitations for producing coatings such as TiAlN and multi-layer coatings. A photograph of a system manufactured by Metaplas-Ionon is shown Fig. 7.4.

Vacuum Arc Deposition

In arc deposition, the vapour source is the anode or cathode of a low-voltage, high-current electric arc in a good vacuum or low-pressure gas [Gorokhovsky 1998]. Arc deposition technology was first developed in the Soviet Union. This was apparently a serendipitous discovery, when engineers working on a Titanium sputter pump discovered that metal objects inside the chamber were coated by the familiar gold coloured titanium nitride.

In the low voltage cathodic arc [Boxman 1995 Brown 1998] the evaporation is from a series of short duration microarcs moving over a solid cathodic surface with typical velocities of the order of 10 metre/sec. The erosion rate is proportional to the current and is a measure as to how many grams of the target material would be evaporated for 1 Coulomb of electrical charge. This value ranges between 10-50 micrograms. 90 percent of the vaporised material as well a good fraction of the background reactive gas species is ionised. The arc spot motion can lead to it wandering to the target edge and extinction. A variety of techniques have been discovered to stop arc wandering. Most common of them use grooves along the edge, magnetic fields, a ring with high magnetic permeability, a ring with high electrical conductivity and a boron nitride ring.

Conventional cathodic arc produces droplets of metal ejected from the cathode. These droplets can contaminate the coated surface, limiting the cathodic arc coating applications to coatings that do not require high surface finish. Following the pioneering work of Aksenov [Aksenov 1978], a number of techniques have been developed to filter out the macroparticles from the plasma stream. Most of them use the fact that macroparticles follow ballistic trajectories, while the plasma stream can be made to flow along magnetic fields. The toroidal magnetic filter is schematically illustrated in Fig. 7.5. The electrons of the arc plasma get magnetized and follow the toroidal magnetic field lines, dragging the ions along with them. The neutral macro particles follow a straight trajectory and hit the walls and get removed from the stream. The ion trajectory ends on the substrate to be coated.

In the anodic vacuum arc, a thermionic cathode provides the electrons required for evaporating the anode material in the form of a thin wire or solid material contained in a crucible [Ehrich 1990]. This technique provides droplet-free metal vapour, with the vaporised material getting ionised as it passes through the arc plasma. The trajectory and energy of these ions can be controlled as they transit from source to substrate. Control of the deposition energy can lead to coatings having high purity, greater density and adhesion. Electrically biasing the substrate can enhance the metal vapour ion flux. This will also help in improving the adhesion of the coating. Increasing the electrical power deposition at the anode can increase the amount of metal vapour produced. The main advantage that this technique offers is that the coating can be deposited on any substrate independent of its physical, chemical and electrical properties. Also, a range of metal coating can be deposited by simply choosing the required anode material. By appropriate control of the process time and parameters we can obtain coatings of desirable thickness.

Ions produced by vacuum arc also have high chemical reactivity leading to good stoichiometry over a much wider range. This is important when depositing coatings on complex shapes. The arc plasma is effective in ionising the vaporised material as well as the reactive gases used in reactive deposition. Ions of the film material can be accelerated to a high energy before being deposited. Reactive gases are activated in the plasma to aid in reactive deposition processes. Poisoning the cathodic surface during the reactive arc vapour deposition is much less of a problem than with reactive sputter deposition. The main disadvantage of arc vapour deposition is the presence of molten globules ejected from the electrode can be deposited in the film, leaving nodules on the surface.

Many manufacturers in Europe, North America and Japan supply industrial scale vacuum arc coating systems. The basic components of a vacuum arc coating system consist of a vacuum chamber, cathode assemblies, arc power supply systems, bias power supply, control panels, water-cooling system, compressed-air supply system, and a vacuum pumping system. Macro particle filters are optional for relatively high quality coating.

The coating chamber is either cylindrical or box shaped made of stainless steel with a double wall for water-cooling [Boxman 1989]. A front door for loading and unloading also provides access for cleaning and maintenance. View ports are mounted on the front door for visual inspection. A shutter behind the view port keeps the glass window clean from vapour deposition during operation. Cathodes are mounted on the sides of the chamber wall. A typical system has a number of cathodes in order to achieve optimum uniformity of coating. The back of the coating chamber is connected to the pumping system. The pumping system consists of mechanical and diffusion pumps. The automatic pressure controller maintains a constant gas pressure in the chamber during deposition. The fixturing system, including a planetary rotation system for racks, is mounted on the top. The planetary rotation system supports a number of fixturing posts and is driven by a variable-speed motor providing two degrees of motion for each of the fixturing posts, self-spinning as well as circling around the chamber. Consequently, uniform coating is achieved. Manufacturers, however, differ in the preferred mode of arc motion control.

A bias power supply provides electrical potential bias between the cathodes and the substrates. The charged particles emitted from the cathodes are accelerated in the electric field and get deposited on the substrate with high kinetic energy. This kinetic energy enhances adhesion. The bias power controller has an arc suppression circuit to minimise local area arcing, which may damage the quality of the coating.

An arc-power-circuit-supply controller for the cathodes has multiple sets of controllers, one for each cathode. The voltage between the anode and cathode is about 20 V depending on the anode-cathode configuration. To sustain the arcing, the minimum current is about 40 amps and 60 amps for Titanium and Zirconium, respectively. While low current is preferred for fine-grain-size deposit, the drawback of low current is that the arc spots travelling on the surface of the target are not stable and extinguish easily. However, the arc can be restarted automatically.

Multi-Arc, with coatings based on cathodic arc technology, offer a wider range of coatings such as TiN, TiCN, TiAlN, ZrN, ZrTiN and CrN. Major sales would probably be in TiN, TiCN with anticipated growth in TiAlN. Hauser Techno Coating in Holland also offers arc technology concentrating on TiN, TiCN and CrN. The arc coating technology has always been viewed as the PVD technology with potential for development because of the inherently high ionisation levels and ease with which multi-layers can be developed. In fact, anodic arc coaters have been used for high speed barrier layer coating of plastic webs and bottles.

Magnetron Sputter Coating

Sputter deposition [Grove1852] is a PVD process in which the coating material is atomised by sputtering. An energetic particle striking a solid can transfer its momentum to the target material, resulting in atoms being ejected from the surface of the target. At moderate energies in the range of several hundred eV through several keV, the incident particle can cause substantial numbers of near-surface broken bonds, atomic dislocations, and ejection or sputtering of atoms. Sputtering deposits atoms with energies in the range of 4.0 to 10.0 eV onto the substrate. Sputtering also enables alloys and compounds to be readily deposited without change in composition.

Sputter deposition can be performed in a vacuum or at pressures low enough that the sputtered particles do not suffer gas-phase collisions in the space between the target and the substrate. At higher gas pressure (5-15 mTorr) energetic particles that are sputtered are “thermalized” by gas-phase collisions before they reach the substrate. Reactive and non-reactive routes can form sputter-deposited films. Non-reactive sputtering is carried out in inert gas plasma; usually argon. Reactively sputtered films can be deposited using a variety of gases.

Plasmas of inert working gases to which the process gases are added at pressures in the order of 10^{-2} mbar provide the high-energy ions for sputtering. They bombard the cathode, which is designated as the target. The oldest configuration is a diode plasma formed when a relatively large potential is applied between two electrodes immersed in a gaseous medium. DC sputtering may be used to deposit metal thin films at high rates, or oxides or nitrides with a reactive background gas. RF-diode sputtering, on the other hand, uses an oscillating power source to generate sputtering plasma. RF sputtering may be used to deposit metal or insulator thin films in inert or reactive atmospheres. Triode sputtering utilises a third electrode in the form of a simple biased conductor or a thermionic electron source to enhance ionisation.

Modern industrial coating systems employ magnetron sputtering and are carried out at pressures below 0.1 Pa and high target power densities above 30 W/cm^2. The high sputtering rates attainable in magnetron sputtering allow reactive deposition of compound films as long as the sputtering target is not ‘poisoned’ by reacting with the gas to form a low-sputtering rate compound. Magnetron sputter deposition is a line of sight collision less process and produces films with compressive stress.

Low-pressure magnetron devices use magnetic fields to produce good plasma confinement to increase the plasma density near the cathode surface and to enhance the sputtering rate. A magnetic field, with field lines starting and ending on the cathode surface and transverse to the electric field is used to trap the electrons. The electric field is always oriented normal to the surface of the cathode. This results in a E x B drift for electrons, which gives rise to a sequence of cycloidal hopping steps parallel to the cathode face. If the magnetic field lines originate and terminate on the surface, the energetic electrons travel along the field lines and get reflected at the mirror regions. As a result, the secondary electrons, which are emitted from the cathode because of ion bombardment, are confined to the near vicinity of the cathode. The transverse magnetic field is configured so that the E x B drift paths form closed loops, in which the trapped, drifting electrons are constrained to circulate many times around the cathode. The common geometries for this are circular or racetracks. This produces a high-density plasma region above the target surface. However, substrates positioned outside this region get reduced ion flux.

By adding another pair of magnets [Windows1986], the field lines can be partially diverted enhancing plasma flow towards substrates kept away from the target region. Field shaping can be done by either electromagnets, or a combination of electromagnets and permanent magnets. This is called the unbalanced magnetron. With the increased plasma density near the substrates higher ion flux can be collected which improves deposition properties.

Unbalanced magnetron is a leaky trap since the plasma can be lost through the opened up field lines, which intercept the walls. An even number of unbalanced magnetrons [Sproul 1990, Rohde 1990] can be used for closing the field lines and creating a field free region equidistant from the magnetrons. The field configuration acts as a magnetic multipole bucket trapping the plasma and immersing the substrates in the diffused plasma as shown in Fig.7.6.

Sputtered metal atoms are isotropic and result in poor deposition. If the metal atoms are ionised and accelerated to energies significantly greater than their thermal energy, the ions will arrive normal to the surface. If the ionisation fraction is made high, the deposition will be primarily directional and the utilisation of the sputtered atoms from the cathode will be high. Additional gas ionisation [Rossnagel 1993] results in intensified discharges and high rate magnetron sputtering. In the late 1980s and early 1990s, systems were specifically fabricated to optimise the relative ionisation of metal particles prior to deposition. This latter technique has proven to be the most robust for coating applications thus far. This can be done by using hot cathode discharges, hollow cathode electron source, inductively coupled RF source or microwave source. Additional ionisation not only provides a higher plasma density near the target region, but also increases the ionisation of the sputtered particles.

The operating scheme [Rossnagel 1994] is as follows. Auxiliary plasma is generated in the region between the magnetron plasma and the sample. As the sputtered atoms pass through this plasma, some fraction of them are ionised by electron bombardment during the transit. The ionisation fraction can be high because the ionisation potential for the metal species is typically 5-7 eV, whereas the ionisation potential for the inert gas species like Argon is 15.7 eV. The relative flux of metal atoms is small compared to the density of the inert gas atoms (typically 1-5 per cent). The metal ions drifting back toward the cathode sheath are accelerated by the magnetron voltage and are used to sputter more atoms from the cathode. The efficiency of utilisation of the sputtered metal atoms can also be quite high.

The relative ionisation of the sputtered atoms at the sample location is a function of several parameters. First, it is sensitive to the density of the auxiliary plasma, which is itself dependent on a number of parameters. In addition, the metal-ionisation level is dependent on the residence time of the metal atoms in the plasma. At low pressures, the sputtered atoms transit the plasma region rapidly, and the ionisation level is low. As the pressure is increased to several tens of mTorr, the sputtered atoms are slowed by gas collisions. As a result, they spend more time in the discharge and are more likely to be ionised. The optimum pressure depends on system dimensions, but typically is in the 15-30 mbar range, which is much higher than would be used for conventional sputtering.

Another direction of development of industrial coating system is the use of self-sputtering [Hosokawa 1980], where, the inert background gas is avoided, and the sputtering is performed by the ionisation of the sputtered species themselves.

Compared to the evaporative PVD, sputtering is a low temperature process allowing proximity of the source and temperature-sensitive substrates. Furthermore, the target can have any orientation since there is no molten pool. Elements, alloys and compounds including refractory materials can be deposited using this technique. The sputtering target provides a stable, long-lived vaporisation source. In some configurations, the sputtering source can be a defined shape such as a line or the surface of a rod or cylinder. Reactive deposition can be easily accomplished using plasma-activated reactive gaseous species. The target areas can be scaled up enabling economical large area deposition.

Although sputtering is more controllable than evaporation it is an energetically inefficient process to produce metal vapour with energy costs typically 3 to 10 times that of evaporation. Particle flux is low in sputtering compared to what can be attained in thermal evaporation. In many configurations, the deposition flux distribution is non-uniform, requiring dynamic fixturing to obtain films of uniform thickness. Sputtering targets are often expensive and material use may be poor. Most of the energy incident on the target becomes heat, which must be removed. In some cases, gaseous contaminants are “activated” in the plasma, making film contamination more of a problem than in vacuum evaporation. In reactive sputter deposition, the gas composition must be carefully controlled to prevent poisoning of the sputtering target.

The cathodes are typically rated at 20-30 kW though there is no fundamental plasma limit to this power rating; it is limited primarily by the ability to cool the cathode by means of flowing water. The power supplies are switching supplies, typically ganged together in modular fashion. The supplies have fairly sophisticated arc-detection and -suppression circuitry to reduce unipolar arc formation, which can result in spitting of microscopic droplets onto the wafer substrate. Dual polarity devices with two magnetrons acting sequentially as cathode and anode are increasingly being used for dielectric film coating.

The cathode materials currently used are generally Al (0.5 per cent Cu), Ti, Ta, and Cu. The purity is generally 99.99 per cent for the Ti and Ta cathodes, and 99.999 per cent or higher for the Al (Cu) and Cu cathodes. The high-purity disks, typically about 1-cm thick, are diffusion-bonded to Al or Cu backing plates, which form the vacuum seal as well as the cavity for both the magnets and the water-cooling. The cathode plate must be insulated from the grounded vacuum system, and this is achieved by means of a 1-cm-thick ceramic ring and O-rings. These large-diameter O-rings (typically 14-in. diameter x 1/8 in. thick) limit the base vacuum pressure of the deposition chamber to the 10^{-8} Torr range.

Ion plating

Ion plating combines the PVD techniques described above with energetic ions bombarding the surface during coating. The ion bombardment during the growth of the film provides energy to the atoms arriving on the surface and allows them to move around and find energetically favourable sites. This ion massaging modifies and controls the composition and properties of the deposited film and improves surface coverage, adhesion and coating density. There is continuous sputter erosion during deposition resulting in a cleaner, more adherent deposit. High gas pressure results in greater scattering of the vapour and a more uniform deposit on the substrate. Recent research suggests that beyond a critical energy, the ion plating is benefited from higher flux of ions on the surface.

The energetic particles used for bombardment are usually ions of an inert or reactive gas or ions of the depositing material. Ion plating can be done in a plasma environment where ions for bombardment are extracted from the plasma, or it can be done in a vacuum environment where ions for bombardment are formed in a separate ion gun. The latter ion-plating configuration is often called ion beam assisted deposition (IBAD). Figure 7.7 shows an arrangement for ion plating.

Ion plating has a number of attractive features. By injecting significant energy into the surface of the growing film, atomic packing can be densified. Surface coverage can be improved over vacuum evaporation and sputter deposition due to sputtering/redeposition effects. Film properties such as adhesion, density, residual stress, optical properties etc. can be modified. Film properties depend less on the angle of incidence of the flux of material deposited than they do on sputter deposition and vacuum evaporation due to atomic peening and sputtering/redeposition effects. Bombardment can be used to improve the chemical composition of the film material by enhanced chemical reactions and sputtering of unreacted species from the growing surface during reactive deposition. In some applications, the plasma can be used to activate reactive species and create new chemical species that are more readily adsorbed to aid in the reactive deposition process.

With many processing variables to control, ion plating is a complex technique. It is often difficult to obtain uniform ion bombardment over the substrate surface leading to film property variations over the surface. Moreover, substrate heating can be excessive. Under some conditions, the bombarding gas gets incorporated in the growing film and the atomic peening may generate excessive residual compressive stress.

Other techniques based on the utilization of ion beams for surface modification include:

Ion stitching

Ion bombardment at an energy sufficient to penetrate the interface between a thin coating and the substrate enhances adhesion by breaking the remaking of inter-atomic bonds.

Ion beam mixing

Coating atoms are transported into the substrate by ballistic processes and by radiation enhanced diffusion, to a depth related to the ion energy.

Ion assisted coating

Simultaneous or sequential deposition and ion bombardment provides a compact and adherent coating with controllable composition and which can be built up to several microns.

Plasma-assisted Chemical Vapour Deposition

Chemical vapour deposition (CVD) involves a gas-phase chemical reaction occurring near a solid surface with the products depositing on that surface. The material to be coated is present in the form of molecules and the vapour in reaction with the atoms or molecules of the workpiece produces films by condensation [Freller 1994]. The gold coloured titanium nitride coating is perhaps the most ubiquitous CVD film. A stable but volatile metal donor gas such as titanium tetrachloride undergoes thermo-chemical dissociation and reacts with Nitrogen released from a metalloid donor gas such as Ammonia. The typical substrate temperatures range form 700 to 1500 degree C. The coating thickness ranges from 1 to 50 microns. The CVD process has good stoichiometry, high density of the deposited layer, excellent adhesion, good throwing power and is easy to apply on three dimensional work pieces. The performance indices of the final coating are determined by a complex interplay between the process parameters and the substrate properties. The coatings deposited by CVD are used in various applications requiring wear resistance, oxidation resistance, corrosion resistance, and electrical, optical, or tribological properties. Depending upon the applications, the characteristics of coatings may be varied by controlling process parameters and species.

CVD processing is generally accompanied by volatile reaction by-products, which along with unused precursor vapours and other processing gases, must be removed from the deposition system. High deposition temperatures are usually required for complete decomposition or reaction. Some precursor material may be expensive or chemically unstable. There are many processing variables such as vapour concentration, gas composition, heating profile and gas flow pattern. Further, incomplete decomposition of the precursors can leave undesirable impurities in the deposited material.

The high substrate temperature has restricted CVD applications to materials such as cemented carbides. The plasma assisted CVD utilises the high chemical reactivity of the plasma environment to overcome the requirement of high temperature [Laimer 1989]. The plasma produced by variety of electrical discharges employing dc, radiofrequency and microwave acts as a catalyst for the reactions even at much lower temperatures [Fig. 7.8]. The relatively lower temperature of the process widens the scope of applicability of the PACVD process to a large range of cutting tools and industrial components including HSS. The term Plasma Enhanced Chemical Vapour Deposition (PECVD) is also applied to this process.

In the TiN PACVD process, nitrogen, hydrogen and Titanium tetrachloride vapour is used as the reactive gas mixture at sub-torr pressure. An abnormal glow discharge is struck in this mixture with a typical current density of a few milliamperes per square cm. The workpiece acts as the cathode and the temperature is controlled to be in the 500^o region. Deposition rate is 1-10 micrometer per hour. The film hardness can be in the range of 2000 kg per square millimetre.

At temperatures below 350^o C, the detrimental effects of chlorine such as production of amorphous TiN-Cl coatings, or formation of ammonium chloride become a serious problem. To avoid these problems a volatile halogen-free precursor such as titanium dialkylamide has been used as the donor [Weiller 1997]. With titanium amides, excited in a plasma discharge, hard titanium carbonitride coatings could be obtained at temperatures below 400^o C. The coating is made up of fine-grained polycrystalline layers with a hardness values of about 2000 HV was obtained, which, although below the typical hardness of 3000 HV obtained by CVD at 1000^o C, is still industrially acceptable

PACVD is not restricted to TiN, but heralds the possibility of new processes to produce deposition of superhard coatings like cubic boron nitride and diamond coatings. Many elemental, alloy, glassy and compound materials can be deposited using PACVD technique. The microstructure of the material can be varied over a large range, sometimes from amorphous to polycrystalline to single crystal. The scaling to industrially meaningful dimensions and expanding the substrate base to industrial tools are being pursued by a number of laboratories. This is especially true for wear-resistant coatings, which perhaps have the highest application potential. Another area of thrust is in lowering the substrate temperatures, which still remain high for a variety of coatings. Of all the plasma assisted techniques, the microwave plasma route appear to offer the most economic and reliable solution to many of these problems which inhibits the penetration of PCVD into industry.

Plasma CVD can be concurrently or sequentially operated with other techniques. One example is the use of sputter deposition of a metal in conjunction with low-pressure, plasma-enhanced CVD of Carbon from Acetylene to deposit metal carbide as a wear-resistant coating on tools. If Nitrogen is present, a carbonitride can be deposited. Varying the ratios of Nitrogen and Carbon in titanium carbonitride deposition can give a range of colours from black to purple to gold. These coatings are used for decorative and wear-resistant applications. Metal organic polymer composite materials can be deposited by a combination of evaporation or sputtering combined with plasma polymerisation of an organic material. A typical configuration for this technique is given in Fig. 7.8.

Thin Film Coated Products

Titanium Alloy Coating

Transition metal nitride, carbide and carbonitride coatings, such as TiN, TiC and Ti(C, N), are predominantly applied by physical vapour deposition to increase tool life as well as quality of the machined surface. The properties of these coatings are listed in table 1. PVD coating of cutting and forming tools by ion plating started in the middle of the seventies and was put to industrial use in the 1980’s with twist drills developed and coated by Balzers, and gear cutting tools by Mitsubishi.

Gold coloured Titanium Nitride is the oldest and the most successful hard PVD coating. With a hardness of about 3000 DPHN (84 RC) it is harder than tungsten carbide and HSS. Claims for improved performance of PVD TiN cutting tools were first publicised in the early 1980’s. The coating offers excellent wear resistance with a wide range of materials and allows the use of higher feed rates and cutting speeds It improves the performance of tools used for cutting, punching, forming and injection moulding operations too. Decrease in galling and welding of workpiece material with a corresponding improvement in surface finish of the work is seen in forming operations. Tool life increases by a factor of two to three. In addition, the coating imparts resistance to abrasion, corrosion, erosion and friction and inhibits welding and galling.

Over the last decade there has been a growing acceptance of this performance benefit by the manufacturing industry. The has been driven by the need for greater productivity from expensive high-performance machine tools and the demand that the cutting tools perform at optimum efficiency giving minimum machine downtime. In addition, demands for improved quality of machined components can be met with coated tools, which, in many cases, can deliver better surface finish, and less sub-surface deformation.

A wide range of steels such as cold working steel tempered over 500^o C, hot working steel, high speed steel cast, high speed sintered steel, hard steel and P30-P40 steels are amenable to PVD coating. The use of coated tools has achieved the most wide- spread application in the field of gear cutting. At least 80 per cent of the gear cutters are now coated with TiN. In 1976, tools for cold extrusion were the first tools to be coated by PVD in Europe. It has been found that welding between the tool and the workpiece can be drastically reduced with a greater improvement in the flow performance.

Dies used for near-net shape production of precision Aluminium parts use considerable amounts of lubricants. They deteriorate the surface quality of the product, lengthens the casting cycle and their disposal poses ecological problems. The deposition of wear resistant coatings offers a way to reduce the use of lubricants in the casting process. TiN and TiC deposited by PACVD process follow the intricate contours of the dies and form coherent interfaces. TiB_2 is especially suited for its low solubility with Aluminium and hence provide excellent corrosion resistance to melts. In fact, coated dies demanded 97 per cent less lubricants. TiN coatings led to a lengthening of the service life of the die by a factor of 45 to 130. Carbon rich TiC coatings led to an increase of die life by a factor of 160.

Titanium nitride is a prime candidate for replacing PVD Chromium coatings. Titanium nitride is much harder than chromium and can be applied in much thinner coatings. Chromium however is preferred for highpoint or line-load applications. Titanium nitride coatings also do not provide as much corrosion protection as do thicker, crack-free Chromium coatings.

Variations in substrate temperature also affect the stoichiometry of TiN coatings. Bias voltage, which controls the plasma assistance has been shown to play a major role in determining the degree of internal residual stress and hence the hardness of coating. The PVD coating properties depend on the nature of the deposition process as well as the deposition parameters used by the coating provider [Benmalek 1991]. For example, coatings deposited using arcs tend to be more textured than those produced by electron beam evaporation and sputtering. Hardness ranged from 1500 HV25 to 3300 HV25 and equally wide variations were seen in the critical loads measured by scratch hardness testing (12.5N to 35.8N).

Performance of TiN is continuously being benchmarked. Commercial PVD systems differ in the method of titanium vapour production, process parameters and configurations, which must inevitably lead to variations in the final TiN coatings. Commercially available TiN coated tools exhibit wide variation in characteristics and properties as well as significant differences in performance. The UK National Centre of Tribology studied the performance of drills in the bright, steam tempered, and TiN coated condition supplied by different coating/tool suppliers and found wide variation in the performance. On average the TiN coated tools showed an improvement of 610 per cent over steam-tempered drills and 2,680 per cent over bright drills. Coatings made from five commercially available PVD methods had the substrate interfacial structures quite different despite having relatively similar microstructures [Hakansson 1991]. These differences were supposed to originate from variations in the pre-treatment and sputter cleaning procedures.

It appears that even after all these years since the coating first appeared in the market, and considerable efforts to bench mark the performance and process aspects, PVD TiN coating on cutting tools is still a subject of research and development.

Zirconium Alloy Coatings

Zirconium nitride (ZrN) and its derivative zirconium carbonitride Zr(C, N) belong to the less investigated materials, even though these coatings, in comparison with the commonly used TiN, have a smaller coefficient of friction while maintaining comparable hardness and chemical properties. These coatings are excellent in the machining of non-ferrous metals such as brass and Ti alloys. The coating is harder than TiN (approximately 3100 Vickers hardness) and has more lubricity, improved chemical resistance, and better thermal stability at higher temperatures. ZrN coated tools are reported to last from two to ten times longer than uncoated tools and up to five times longer than TiN when drilling grey iron and brass. ZrN coated tools oxidise at approximately 600° C.

Chromium Nitride coating

CrN coating obtained by reacting Chromium vapour with Nitrogen atoms, were industrially evaluated first by Balzers in 1990 [Schulz 1991]. The composition can be CrN, Cr_2N, or a mixture of both, depending on the mass flow rate of nitrogen used during the deposition. Compared with TiN, CrN offers a lower coefficient of friction as well as greater resistance to lock-up during movement and is more suitable for tribological applications. CrN also offers greater thermal resistance and acid-base corrosion resistance than TiN.

CrN coating has a fine-grained low stress structure, which permits the deposition thickness to exceed that of conventional PVD coatings [Navinsek 1997]. A Chromium intermediate layer helps to form an optimum width of the interface and improves the adhesion to steel substrate as well as corrosion and oxidation resistance. CrN coatings are superior to other coatings in terms of thermal stability and corrosion resistance, although its hardness is slightly lower. CrN coatings are softer, thicker and less brittle than TiN and are suited to protect relatively softer surfaces like stainless steel, Copper-Aluminium alloys and light metal alloys. In die casting applications and in manufacturing and cold forming of Copper and Titanium, the good performance of CrN at elevated temperatures [Schulz 1992] comes to advantage. CrN can replace environmentally hazardous galvanic coatings [Quaehaegens 1996]. The chemical affinity of CrN to non-ferrous metals has a beneficial effect on the operative behaviour of tools used for machining nickel based alloys, e.g. monel, inconel or forming copper.

Multicomponent Coatings

Hard PVD coatings normally contain a high degree of internal compressive stress due to lattice distortion and thermal mismatch effects. Pinhole defects in thin coatings invariably cause some porosity, leading to accelerated pitting corrosion and failure at the substrate coating interface in aqueous environments. Thin coating fails in conditions of liquid borne particulate erosion.

Work on improving TiN has usually involved adding other elements to the compound to make a multicomponent compound. Adding new elements changes the properties of the deposited film such as increasing the hardness or ability to withstand higher operation temperatures. The next generation of PVD coatings of significance after TiN are TiCN and TiAlN, which are gaining in commercial significance in European, North American and Asian markets. It appears that a wide range of binary and ternary compounds could be vapour deposited for a variety of applications.

The PVD process can produce titanium nitride and carbide mixtures with differing stoichiometry to form bronze coloured carbonitrides [Bergmann 1990]. From the tribological perspective, titanium carbonitrides offer a compromise between the high hardness of the carbide (3600 HV) and the superior thermochemical stability of the nitride. The carbonitrides outperform nitrides at high cutting speeds and offers improved wear resistance with abrasive, adhesive, or difficult-to-machine materials such as cast iron, alloys, tool steels, Copper and its alloys, Inconel, and Titanium alloys. TiCN coating gives higher cutting speeds and feeds and extended tool life when machining, punching or forming higher strength and abrasion resistive steels or non-ferrous metals. The PVD process with Nitrogen and Methane as the reactive gas can produce TiCN coating. With TiCN coating, forming operations with abrasive materials should see improvements beyond those experienced with TiN. Claims for the superior performance of TiCN over TiN in interrupted cutting are based on lower friction characteristics and better heat transfer coefficients. The slower emergence of TiCN as a PVD coating of significance is attributed to processing difficulties, namely, controlling the stoichiometry and residual stress, and choosing the appropriate hydrocarbon carrier gas.

The Purple/black Titanium Aluminium Nitride (Ti,Al)N is a high performance coating which excels at machining of abrasive and difficult-to-machine materials such as cast iron, aluminum alloys, tool steels, and nickel alloys [Knotek 1986, Munz 1986, McIntyre 1990]. The improved ductility of (Ti,Al)N makes it appropriate for interrupted operations. (Ti,Al)N has a higher oxidation temperature than TiN, at 700^{o}C as against 500^{o}C. This feature makes (Ti, Al)N attractive for high speed tooling. TiAlN is growing in commercial significance at a slower rate that TiCN. The reason may be that TiAlN is based on sputtering using alloy target materials, which does not adapt to electron beam systems due to the large differences in melting points between Ti and Al. The possible formation of Al_20_3 on the rake face giving longer tool life at higher cutting speeds than TiN and TiCN may make TiAlN attractive in the future.

Multilayer Coatings

Multilayer coatings, originally developed for optical applications, are entering the tool coating market [Fig. 7.10]. Multilayer coatings would have added toughness and hardness [Holleck 1988] compared to a single component coating since the low energy interfaces would be effective in dissipating energy within the layers as long as there is coherency at the interface. A popular coating developed in Europe [Bergmann 1990] is composed of a base layer of TiN with alternating layers of TiCN with varying CN ratios and a final TiN layer. This coating is supposed to be good for thermal shock. Another multilayer coating idea is to combine both CVD and PVD coating techniques [Quinto 1993]. Combining the tensile residual stress in the CVD layer with the compressive stress in the PVD layer increases the thermal shock resistance and performs well with high speed milling operations.

Nitride superlattice coating is another PVD multilayer coating that looks very promising. The multi-layering of TiN and NbN [Shinn 1992] produced a coating more than twice as hard as either of the coatings when used alone. Indeed, the reported value of 5200 Kgf mm^{-2} approaches the hardness of cubic boron nitride. Maximum hardness values of 5600 kgf/mm^{-2} for single crystal coatings of TiN/VN have been reported [Helmersson 1987] when the superlattice period was in the range of 4-8 nm. The hardness is attributed to restricted dislocation movement due to strain at the coherent interface. Another factor restricting dislocation movement is the small thickness of the layer.

The sputtering technology appears to offer great flexibility for advanced multi-layer coatings. The development of multi-layer coatings is relatively easily carried out using the multiple sources. An interesting recent development is that of combining arc and sputter (ABS) technology by Hauser Techno Coating. Large commercial systems are on the market with the possibility of coating TiAlN, CrN, TiCN, ZrN, in addition to multi-layer superlattices and metal stabilised Carbon. Teer Coatings use multiple unbalanced magnetrons which allow dissimilar metals to be sputtered from pure metal targets simultaneously to form alloy nitrides such as (TiAlN)N, (Ti,Zr)N, (Ti,Al,U)N and (Cr,Zr)N. The attractiveness of this ‘shopping list’ of coatings should be tempered with the commercial realities that viable market volumes have yet to be identified and established for these new coatings.

Nanocomposite Coatings

Nanocomposite coatings [Holubar 2000] represent a new class of films, which, in the simplest case, are composed of two material phases concentrated in very small atomic domains with dimensions typically about 10 nm. The main characteristics of these films are that the number of atoms in the grain is comparable or smaller than the number of atoms in the boundary region surrounding individual grains. The material properties are determined not only by the behaviour of atoms in the grain, but also by the atoms in the boundary. This fact varies the properties of such coatings in a dramatic way compared to polycrystalline coatings.

Superhard Coatings

During the last decade, significant progress was made in the development of a new class of coatings, known generally as superhard coatings. These include mainly the thin-film diamond, cubic boron nitride, carbon nitride and superlattice coatings. These coatings have tremendous potential for significant improvements in the performance of coated components. Although some of these coatings have almost reached the point of commercialisation, they are not yet well established in the metal-cutting industry. The main reason is that the deposition processes have not yet overcome many technological problems for low-cost, reliable coatings.

Thin film diamond coatings have reached the commercialisation stage, and quite a few companies now offer diamond-coated cutting tools for various non-ferrous machining applications. The plasma CVD technique for diamond and diamond-like carbon coating involves dissociation of a hydrocarbon gas in plasma and was originally developed by Whitmell and Williams [Whitmell 1976]. The term diamond-like carbon films (DLC) was first used by Aisenberg and Chabot [Aisenberg 1971] as a description of the hard carbon films that was built up of ordered diamond-like structures of 50 Angstrom in dimension, as shown by the X-ray diffraction pattern. Other diamond-like properties such as optical clarity, high electrical resistivity, chemical inertness was also observed in these films.

The most commonly used deposition methods for diamond coatings include hot filament CVD (HFCVD), microwave plasma CVD (MWCVD) and plasma arc-jet CVD. Other methods, such as laser CVD and combustion CVD have also been applied on a limited scale.

The resulting films are polycrystalline, with a morphology that is sensitive to the precise growth conditions. Growth rates for the various deposition processes vary considerably, and it is usually found that higher growth rates can be achieved only at the expense of a corresponding loss of film quality. Quality implies some measure of factors such as the ratio of sp3 (diamond) to sp2-bonded (graphite) carbon in the sample, the composition and crystallinity. Hot filament and plasma methods have slow growth rates (0.1-10 μm/hr) but produce high quality films.

Thermodynamically, graphite, not diamond, is the stable form of solid carbon at ambient pressures and temperatures. The fact that diamond films can be formed by CVD techniques is inextricably linked to the presence of Hydrogen atoms, the product of dissociation of the hydrocarbon gas.

The surface morphology obtained during CVD depends critically upon the gas mixing ratio and the substrate temperature. Under ‘slow’ growth conditions - low CH4 partial pressure, low substrate temperature - we obtain a microcrystalline film, with triangular {111} facets being most evident, along with many obvious twin boundaries. {100} facets, appearing both as square and rectangular forms, begin to dominate as the relative concentration of CH_4 in the precursor gas mixture, and/or the substrate temperature, is increased. Cross-sections through such microcrystalline films show the growth to be essentially columnar. At still higher CH_4 partial pressures the crystalline morphology disappears altogether; a film which is an aggregate of diamond nanocrystals and disordered graphite develops.

CVD diamond offers many applications. Wear resistant coatings with an ability to protect mechanical parts such as gearboxes, engines, and transmissions, may allow greatly increased lifetimes of components with reduced lubrication. CVD diamond is also finding applications as an abrasive and as a coating on cutting tool inserts. CVD diamond-coated drill bits, reamers, countersinks etc. are now commercially available for machining non-ferrous metals, plastics, and composite materials. Initial tests indicate that such CVD diamond-coated tools have a longer life, cut faster and provide a better finish than conventional tungsten carbide tool bits.

Diamond coated cutting tools are being evaluated for dry cutting applications for Aluminium alloys. This is driven by the large cost component of cutting fluid technology (amortisation, energy, disposal etc) as well as increasing environmental regulations imposed on the disposal of used cutting fluid. It is reported that in addition to increasing costs of cutting fluid disposal, the laws governing their disposal in Germany have increased from two in 1950 to more than thirty at present [Lahres 1997].

Diamond film is deposited at temperatures in excess of 850^0C, which makes it unsuitable for high-speed steel tools. In the case of cemented carbide tools, the biggest challenge was to overcome the deleterious effect of Cobalt binder in the substrate, which tends to graphitize the diamond and destroys adhesion. A variety of techniques have been used to prevent the interaction of Cobalt with diamond film, which primarily depend on chemical methods to remove Cobalt from the surface of the carbide substrate. Manipulation of the carbide surface crystal morphology during sintering has also been used to improve the adhesion of diamond to the substrate.

One of the great challenges facing researchers in CVD diamond technology is to increase the growth rates to economically viable levels in the range of nm /hr without compromising on the film quality. Progress is being made using microwave deposition reactors, since the deposition rate has been found to scale approximately linearly with applied microwave power. Currently, the typical power rating for a microwave reactor is ~5 kW, but the next generation of such reactors may have power ratings up to 50-80 kW. In any application where friction is important the diamond-coated tool bit will heat up and, in the case of ferrous materials (be it the tool substrate or the workpiece) the diamond coating will ultimately react with the iron and dissolve. Another outstanding challenges in the application of diamond film technology - whether as a wear-resistant coating or as a fine abrasive- is in finding suitable barrier layer materials to allow diamond coating to be deposited on iron and steel machine parts.

Another recalcitrant coating process is the deposition of cubic boron nitride on carbide substrates. Apart from the difficulty of synthesising the pure cubic phase of boron nitride, large internal stress in the coating increases with the thickness and cubic content of deposited BN film. This difficulty has prevented the successful deposition of a uniform film of cubic boron nitride of thickness exceeding about a micron. Initially, a combination of different CVD methods (HFCVD+MWCVD, ECR-MWCVD, Laser ablation, etc.) were attempted to synthesise cubic BN, and recently PVD methods are being studied with some success in the laboratory. Essentially the same situation exists for the carbon nitride coatings, which are unlikely to find useful applications in metal-cutting. However, these films show significant promise in other tribological applications.

The superlattice coatings are formed by sequential deposition of ultra-thin layers of two compounds with a close match of lattice parameters, such that they can develop coherent interfaces leading to a superlattice structure. Most of the work in this area has been done on refractory metal nitrides. The most promising of these materials include TiN/NbN, TiN/AlN, and TiN/VN. These coatings are typically deposited by reactive magnetron sputtering and have demonstrated significant improvements in hardness and wear resistance as compared to TiN and other conventional hard coatings.

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Table I : Properties of titanium based coatings

Property	**Titanium Nitride TiN**	**Titanium Carbonitride TiN(C,N)**	**Titanium Aluminum Nitride (Ti,Al)N**
Colour	Gold	Bronze	Purple / Black
Hardness	2800HV	3000HV	2800HV
Coating Thickness	2 - 4 microns	2 - 4 microns	2 - 4 microns
Thermal Stability	550°C	400°C	750°C
Lubricity TiN/Steel	0.4 - 0.55	0.5 - 0.6	0.4 - 0.6
Deposition Temperature	500°C	500°C	500°C
Cost Comparison	Base	1.5 x Base	2 x Base

Hard Coatings for Cutting Tools Deposited by CVD and PVD Techniques

COATINGS	**CVD**	**PVD**
Carbides	TiC, WC	TiC, B_4C, Cr_xC_Y, ZrC, WC
Nitrides	TiN, ZrN, HfN	TiN, ZrN, CrN, NbN, VN, TiAlN
Carbonitrides	TiCN, ZrCN	TiCN, ZrCN
Oxides	Al_2O_3, ZrO_2	Al_2O_3, ZrO_2
Multilayer Coatings	TiC/TiN,TiCN/TiN, TiC/Al_2O_3, TiC/Al_2O_3/TiN,TiCN/ Al_2O_3,TiCN/Al_2O_3/TiN, [TiCN/Al_2O_3]n	TiCN/TiN,TiAlN/TiN,TiN/ NbN (superlattice coating)
Multiphase Coatings	$Al_2O_3 + ZrO_2$	MoS_2/TiN, MoS_2/Metal
Other Coatings	Diamond, TiB_2, cBN	MoS_2,WS_2 (lubricant coatings), Hard DLC(a-C)

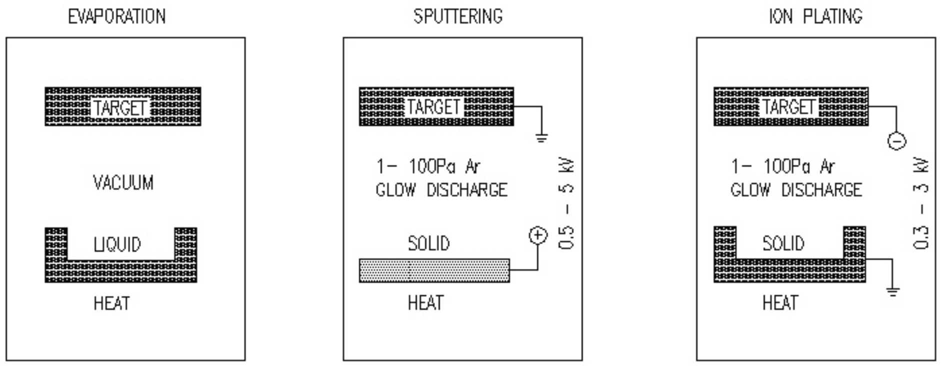

Fig. 7.1. Basic physical vapour deposition techniques

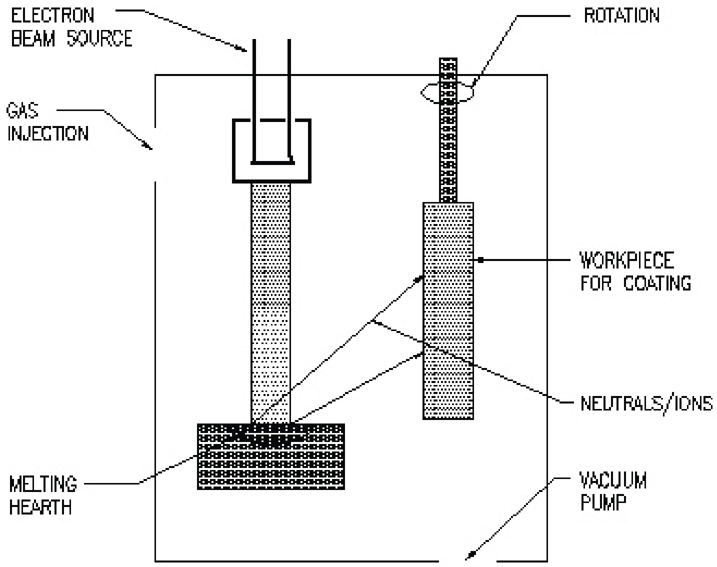

Fig. 7.2. Schematic diagram of Electron beam assisted PVD technique

Fig. 7.3. Photographs of Balzers PVD systems (Photo courtesy Pfeiffer, India)

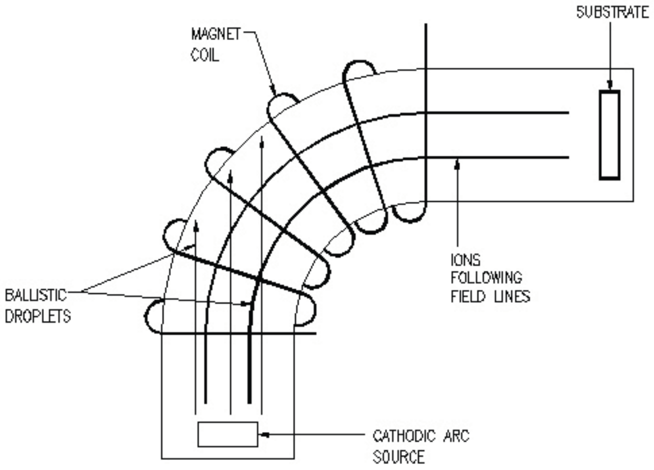

Fig. 7.5. Macroparticle filtering technique for vacuum arc deposition. The macroparticles following a ballistic trajectory are lost to the wall. The ions follow electrons, which are guided by the curved magnetic field.

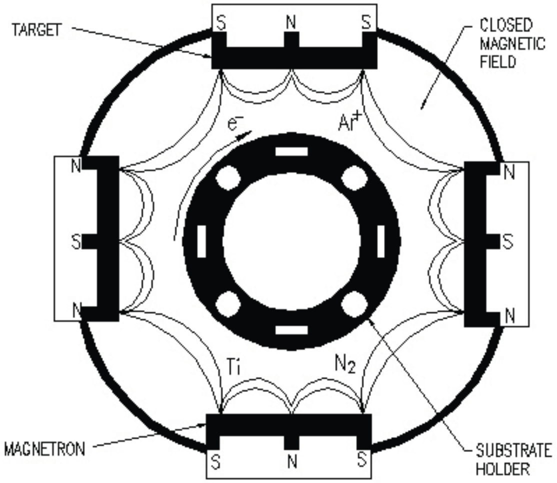

Fig. 7.6. Closed field magnetron sputter deposition system. The ion flux accumulates in the central field-free region where substrate for coating is placed

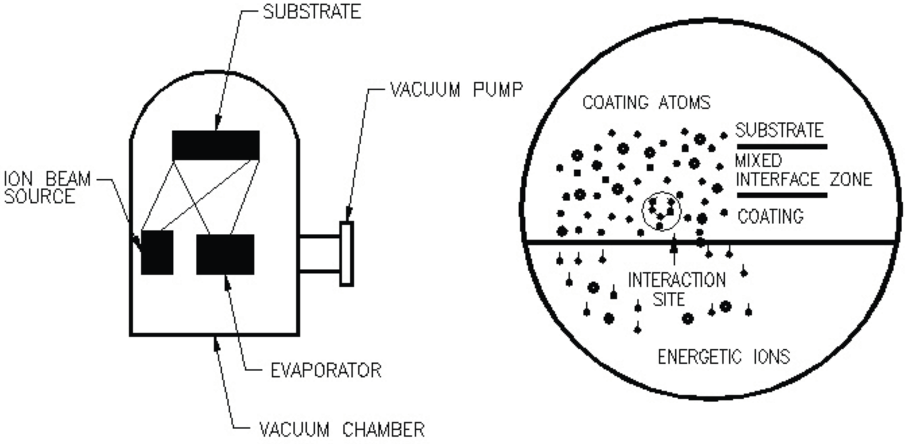

Fig. 7.7. Schematic diagram of ion beam assisted deposition. The ion beam concurrently bombards the coating while the film is being deposited

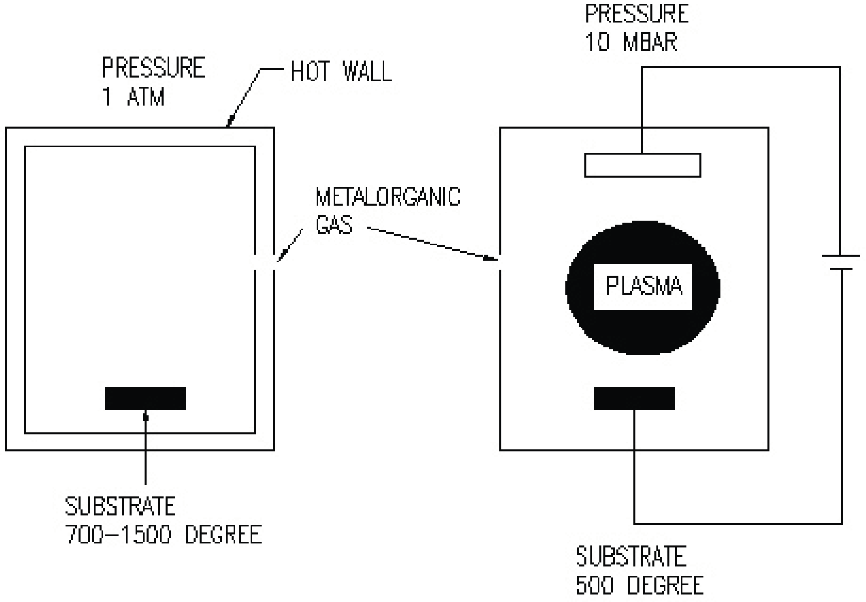

Fig. 7.8. The plasma enhanced CVD process

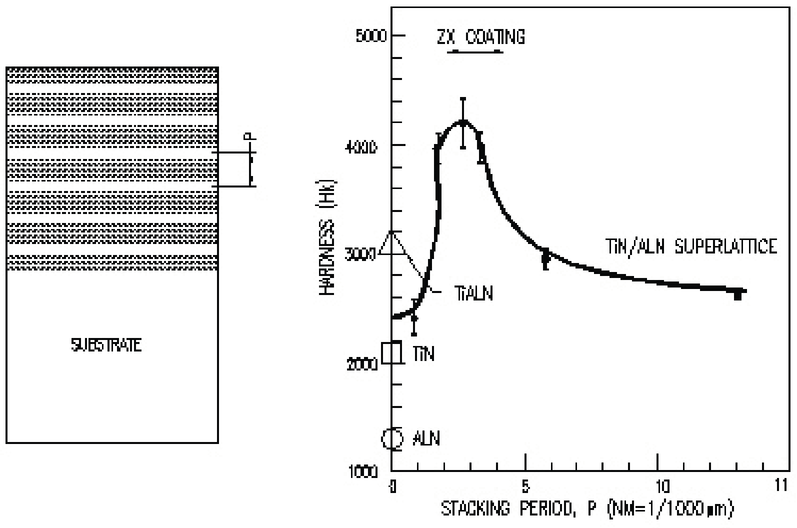

Fig. 7.10. In the multilayer films, many layers of controlled thickness are sequentially deposited

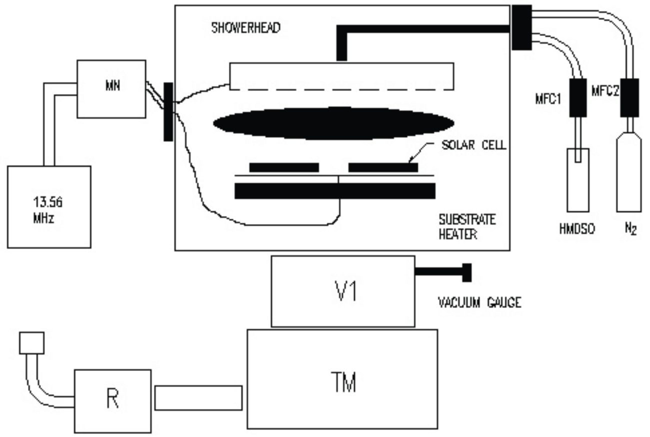

Fig. 7.9.Schematic diagram of a plasma polymerisation system

8. The Plasma Washing Machine

Precision Cleaning of Surfaces

Plasmas can clean surfaces using irradiation with energetic ions or by initiating chemical reactions using radicals. This technique is now finding increasing application for a variety of sophisticated industrial processes where extreme cleanliness of the surface is essential. Biological decontamination of surfaces and environment is also an emerging application. This chapter discusses the basic processes and applications with regard to a few specific areas.

Cleaning as an Industrial Process

Physical surfaces are invariably contaminated by a variety of processes [Adamson 1990]. Gas molecules adsorb on a surface due to the weak Van der Waals forces between the molecule and the surface that arise from interacting fluctuating dipoles. This process called physisorption is characterised by enthalpy changes of the order of 20-25 kJ/mole. Energies of physical adsorption are of the same order as latent heat of evaporation and range from 0.1 to 0.5 eV per atom. These layers can be removed by moderate heating.

Extraneous molecules can form a stronger bond with surfaces through chemisorption. This is due to the formation of a chemical bond between an atom or a molecule and a surface often resulting in structural transformation of the adsorbed molecule. Chemisorption energies are of the same order as chemical reaction energies and range from 0.5 to 5 eV per atom. Enthalpies of chemisorption are in the 200 kJ/mole range. The chemisorbed species may retain their molecular form (associative chemisorption) or dissociate into their component atoms or radicals (dissociative chemisorption). Chemisorbed layers require high temperature or energy for their removal. Fig. 8.1 illustrates these processes schematically.

Surface oxidation is another process, which results in tarnishing and corroding of a surface. The initial stage of oxidation requires a supply of atomic Oxygen, together with sufficient mobility of metal atoms on the surface [Duke 2001]. On many surfaces, an intermediate surface oxide phase precedes the formation of the passivating oxide film, which has a typical thickness of 2 to 3 nm. Some Other surfaces oxidize directly from the chemisorbed state. In addition, films of organic oils, fluxes or polymers and deposition of microscopic particles and microorganisms can also contaminate surfaces.

Surface cleaning can be defined as removing extraneous non-integral material that may deleteriously affect a process or functioning of a product. Cleaning is an essential step in many advanced manufacturing processes. In industrial cleaning, undesirable material from the surface of a part or component must be removed at minimal expense and effect on the environment. Areas of application range across metal processing and machining, surface modification of tools, electronics, jewellery, plastics and glass, optical industries and medical products. Moreover each application has its own definition of the scope and standard of cleanliness.

Cleaning requirements are specific to each application and can range from highly sophisticated ones to the most trivial. The purpose of cleaning ranges from cosmetic cleaning of consumer goods to precision cleaning of surfaces preceding analytical characterisation. Cleaning for the purpose of improvement of adhesion of coatings, bonding of materials, painting and printing is another large segment. Removal of corrosive or toxic materials as well as descaling is another type of cleaning extensively used in chemical industries. Attainment of ultra high vacuum in fusion devices and particle accelerators is critically dependent on the removal of many monolayers of adsorbed gases, especially water vapour and Oxygen from the vacuum vessel wall.

The traditional cleaning procedure involves the use of water, detergents, solvents, chemicals and mechanical methods. These techniques are most economical means for removing large quantities of dirt. The act of cleaning is very often the result of chemical and physical action in combination. Chemical action includes solubilization, emulsification, complexing, filtration and displacement whereas physical action may involve high-pressure sprays, ultrasonic and centrifugal agitation. In all cleaning processes, optimised chemical action has to precede the physical action to ensure effective cleaning without incurring the expenditure of large amounts of energy.

Drivers for Advanced Cleaning Techniques

Traditional aqueous and solvent based cleaning, though apparently cheap, has significant energy and environmental price (Quitmeyer 1994). Drying is slow and requires considerable expenditure of energy. Solvent cleaning is economically more attractive. Low surface tension eases penetration and wetting. Low boiling point solvents are required for vapour degreasing and vapour phase drying, reducing the energy cost. Most solvents are however inflammable, toxic or carcinogenic. There are hidden costs in safety training, liability for employee illness, waste analysis and destruction.

However, all conventional techniques leave a recalcitrant residual monolayer of contamination on the surface, which may require a more refined method of cleaning. Precision cleaning aims to remove the last few layers of any contamination, particularly organic hydrocarbons and chemisorbed layers which might have been left on the surface. This is especially important when applications such as adhesive bonding applications requires a hyper-clean surface where as little as one atomic layer of organic contamination may be detrimental. Many manufacturers already have discovered that it makes no sense to use large quantities of solvents and acids just to remove such thin surface films. Precision cleaning thus has significant economic dimensions that require a balance between the chemical and physical actions.

Chlorofluorocarbons (CFC) are commonly utilised by many industries to remove hydrocarbon oils, greases, and other contaminants from material substrates without leaving potentially damaging residues. Some CFCs photo-dissociate in the atmosphere by absorbing ultraviolet light, releasing fluorine. Fluorine, however, can destroy the atmospheric ozone, which shields the earth from ultraviolet radiation from the sun. Another cleaning agent, Perfluorocarbons (PFC) resides in the atmosphere for as high as 5000 years and can reach the stratosphere in course of time. These also have high global warming potential [Bojkov 1995]. Gases such as C_nF_{2n+2}, NF_3, and others have global warming potentials much greater than CO_2 due to long atmospheric lifetimes and many low energy vibrational modes. Additionally, these feed gases generate F_2, C_nF_{2n+2}, HF, and other species that are both health hazards and difficult to remove from the process effluent stream.

Subsequent to the Vienna Convention on the Protection of the Ozone Layer, organised by United Nation’s Environmental Programme (UNEP) in 1985, The Montreal Protocol on Ozone Depleting Chemicals (UNEP 1987) has mandated ban of CFC production by the end of 1995 and the replacement of cleaning solutions based on Chlorofluorocarbons (CFC) by safer alternatives. Although several such chemicals are available, their effectiveness at removing organic contaminants is less than optimal. Additionally, many alternatives pose environmental, health or safety risks as well as increased cost.

Over the past 50 years, painting and surface treatment industries have been under constant pressure to reduce solvent usage in their process step. Aqueous cleaning in semiconductor manufacturing is a voracious water consumer. More than 2000 gallons of ultrapure water are needed to make a 200 mm wafer. Since the typical fab makes 1500 wafers per day, the total water requirement comes to 3 million gallons per day. The next generation 300 mm wafers would need about 5 million gallons per day, as much as needed by a small city [Pacific 2000].

The detrimental environmental impact of the chemicals used in traditional cleaning techniques is a strong driver for plasma assisted cleaning as an effective alternative to chemical cleaning processes and allows the removal of surface contamination from material substrates while creating no undesirable health or safety problems.

Precision Cleaning Techniques

There are several quality indices for a cleaning process. Some of them are: short process time, ultimate cleanliness of the surface, homogeneity of the surface after cleaning and low influence on the substrate material. The process is defined as cleaning if the residual oil or carbon level is in the range of 500 mg/m^2, fine cleaning if the residue is of the order of 50 mg/m^2 and ultra fine cleaning if the residue is in the range of 5 mg/m^2 [Kegel 1999]. An arsenal of advanced cleaning techniques has evolved to meet the ever-increasing sophistication of the cleaning technology. Solvent-free cleaning technologies can be broken into three main families; chemical, mechanical and physico-chemical. Physico-chemical methods are particularly promising and include ultrasound, plasma, lasers and supercritical CO_2

Ultraviolet light in conjunction with ozone or hydrogen peroxide is used to oxidise an organic material. Both gases can be dissolved in water and when irradiated by the UV light, they decompose. Cleaning action occurs as a result of free radical formation following decomposition and the release of atomic Oxygen, which is a powerful oxidant transforming organic material to carbon dioxide and water in a multi-step process.

Laser cleaning employs energetic laser radiation from UV lasers such as krypton fluoride. The electrons from the surface contaminants absorb energy from the laser and get excited. During the relaxation process, energy is released, which is absorbed by the surface and results in detachment of the adsorbed contamination. Laser treatment can clean organic contamination, epoxy layers and oxide layers from the surface.

Blasting a surface with solid carbon dioxide (dry ice) pellets is a nonabrasive form of physical cleaning. The ice is converted to gas on contact with the surface. Most organic material dissolves in CO_2. Liquid CO_2 can dissolve contaminants, though high pressures are required to maintain the gas in the liquid form. CO_2 can pass through a triple point where solid, liquid and gaseous phases meet, forming CO_2 snow. This medium is used to remove hydrocarbon and silicon oil, fluxes, plasticisers, lubricants etc. Instantaneous momentum transfer by the snowflakes and chemical action of the liquid combine to produce effective cleaning. At high pressures (above 72.8 atm) and low temperature (below 31° C), CO_2 becomes supercritical, combining the liquid and gaseous phases. Supercritical CO_2 has low viscosity and surface tension and penetrate into small pores and crevices thereby enabling ultrafine cleaning of surfaces.

Plasma Assisted Cleaning

Plasma surface cleaning was originally developed to clean ultra high vacuum systems used for fusion research devices and high-energy particle accelerators. Water vapour is an ubiquitous contaminant in such systems. The bonding energy of water molecules to the surface is of the order of 1.5 eV and the thermal desorption rate of water vapour is very slow resulting in prolonged baking cycles before attaining ultra high vacuum. Surface bombardment by energetic particles produced in cleaning discharges was found to be very efficient in removing such contaminants.

Plasma cleaning exploits the ability of plasmas to produce reactive ion species and radicals at low gas temperatures through reactions generated by non-equilibrium electrons. The basic processes are schematically shown in Fig. 8.2. Energetic reactive species generated in the plasma bombard surfaces to cause sputtering, thermal evaporation, or photodecomposition. The specific cleaning action mediated by plasma is based on physical or chemical varieties of sputtering and etching.

In physical sputtering, the impulse imparted by energetic ions bombarding the surface can cause displacement of the atoms on the surface or in some cases, sub-surface. This process has no selectivity. In chemical etching, the reactive species from the plasma react with surface atoms and molecules and produce a volatile reaction product, which can be pumped out [Fig. 8.2]. This has high selectivity since specific chemical reactions can be triggered by the selection of process parameters. However, the process proceeds in all directions and hence is isotropic. In ion-enhanced etching, energetic ions impinging on a surface produce defects, dislocations or dangling bonds on the surface. These defects enhance the surface chemical reactivity and results in chemical etching. This process has both selectivity as well as directivity.

In all these processes, the bond between hydrocarbon and the substrate is modified in such a way that it is more energetically favourable for the organic compound to detach itself from the sample surface [Mattox 1994]. Once detached, the molecular species can be swept from the surface using an inert gas flow. Plasma supplies this bond-breaking energy through optical radiation, neutral particle fluxes or charged particle bombardment. This energy is absorbed by the hydrocarbon and subsequently dissipated by a variety of secondary processes and it is these processes, which give rise to the desired surface cleaning. Plasma is prolific in generating UV radiation, which is strongly absorbed by polymers and results in the formation of free radicals, which tend to be active sites and can readily react with gas components of the plasma. Charge exchange neutrals, generated by the reaction of fast ions with the ambient neutral gas, bombard the sample continuously and impart energy in kinetic, vibrational, dissociation and excitational modes. The kinetic and vibrational modes tend to mildly 'heat' the surface. The dissociative and excitation modes create free radicals. Lastly the charged particle flux carries kinetic, vibrational, and electronic energy, which can impart heat. If the energy exceeds a threshold, it may also cause sputtering. In the process it an also create free radicals.

Apart from the obvious sputtering process, which is akin to a mechanical removal of the surface contaminant, the formation of free radicals is the most important step in the removal of hydrocarbons. These free radicals can involve a number of species including O, OH, H and C bonds. The exact process depends upon the specific hydrocarbon present. We can however outline the process, which occurs as one of the following:

$$RH — P^* + H^*$$

$$RO — P^* + O^*$$

$$ROH — P^* + OH^*$$

Here RH, RO, ROH, are symbolic representations of the various hydrocarbons having a low energy bond to H, OH, or O while P* the product free radical which results once the H, OH, or O bond has been broken by the energy transferred by the plasma. Once a free radical is formed the released components (H, O, OH) can combine with other species and form CO, CO_2 and/or H_2O, all of which are readily removed from the system by the continuous gas flow. Clearly there are numerous intermediate steps in the break-up of the hydrocarbon. Eventually all the C, H and O bound in the original hydrocarbon are converted into gases and thereby removed from the specimen surface.

Because the hydrocarbon can in effect also be the source of it's own oxidant, inert gases (Ar, N_2, H_2…) can be used for the plasma as well as reactive gases (O, CF_4…). The advantage of employing a reactive gas such as O_2 is in the speed of the conversion of the hydrocarbon to a gaseous phase since the C + O à CO reaction can be a rate-limiting step. Employing only inert gases such as Argon sometimes produces a milder and more controlled process. The semiconductor industry uses even more aggressive gases such as CF_4, NH_3, and SiH_4/N_2O.

Photolysis of molecular Oxygen by intense UV radiation at 172 nm produces atomic Oxygen and ozone. Hydroxyl radicals are also produced if water vapour is present. Surface bound hydrocarbons are oxidised by these species in heterogeneous reactions. In halogenated hydrocarbons, the dominant reaction pathway consists of hydrogen abstraction or direct photolysis, oxidation of the hydrocarbon radical and fragmentation of the unstable carbonyl products (Falkenstein 1997). Repeated reactions of this type finally produce carbon dioxide and water. Powerful UV sources based on dielectric barrier discharges that emit the Schumann-Runge band with radiation efficiency of 10 per cent are commercially available for photolysis cleaning applications (Falkenstein 1999).

Plasma treatment can also be used to enhance aqueous cleaning methods. Plasma drying is an excellent complement to aqueous based cleaning systems. Part geometry and surface roughness may increase the difficulty associated with removing moisture after aqueous cleaning. Porous materials are difficult to dry under the static vacuum conditions present in most conventional vacuum ovens. Plasma drying removes moisture faster than conventional methods. Water on a materials surface is exposed to reactive species in the plasma and may be ionised. As plasma treatment is a dynamic process, a laminar gas flow continues throughout the process, removing both ionised and surface water. The plasma drying process operates at a lower pressure than is typical for conventional vacuum ovens. Additionally, a small increase in material temperature during processing aids in removing surface moisture. However, the dynamic vacuum conditions used in plasma treatment coupled with the ability of the activated species to penetrate the pores of the material provided the fastest and most thorough drying process - investigations show that ninety percent of the water was removed within 20 minutes.

Plasma drying technology is especially suited to treat temperature sensitive materials that are damaged when subjected to elevated drying temperature. For some materials such as Kevlar plasma treatment provides both surface cleaning and activation as well essential material drying before further processing.

A broad spectrum of plasma cleaning applications has emerged and has been adapted for metal, polymer and ceramic surfaces, removal of metal residue from hybrid circuits and printed circuit boards, cleaning and sterilisation of bio-medical implants, cleaning of silicon wafers and for restoration of archaeological artefacts. Plasma also eliminates the dangers associated with wet chemistry and has the major advantage over other cleaning methods because there is no liquid waste.

Plasma Cleaning Reactors

Choosing a proper plasma source is a critical element to meet all these requirements simultaneously. Plasmas excited by RF and microwave discharges have emerged as the most appropriate sources for these applications as these produce self-negative biasing of the substrate resulting in non-thermal ion energy bombardment of the surface producing rapid cleaning action. RF and dc arc atmospheric pressure plasmas are also being increasingly applied for plasma cleaning. Though there is no generic design for plasma cleaning systems, the following sections describe some popular reactors.

The instrumentation required for low pressure reactors [Fig. 8.3] includes a reaction chamber, a power supply, and a vacuum source. The sample is put into the chamber, which is evacuated by the vacuum pump. Gas is introduced into the chamber and converted to reactive plasma by the power supply. The plasma reacts at the surface of the sample and volatile by-products are removed by the vacuum pump. A recent development is a box style chamber with internally mounted removable shelves. By selecting and positioning shelves that are grounded, powered, or at a floating potential directional (RIE), downstream, or direct plasma can be chosen. Directional plasma, also called Reactive Ion Etching (RIE), is an aggressive form of plasma [Lehmann 1978]. It offers the benefit of fast etching rates and high uniformity. Direct plasma is less aggressive, but the sample is immersed in the plasma. Downstream plasma is a mild process and is suitable for removing thin films of 10-50 angstroms.

Atmospheric Downstream Plasma (ADP) source contains two electrode units directed upward and toward each other with an angle of about 90 between their axes. Each unit consists of an electrode placed inside a mini-chamber with a water-cooled orifice. When a DC field is applied between the two electrodes, a plasma arc is formed that exits the orifice of one electrode unit and enters the orifice of the other. The plasma is kept from the chamber walls by the flow of mainstream gas.

External magnetic fields direct the plasma arc from its initial path so that a portion can be extended vertically. The increased resistance of the extended path length further heats the resultant plasma region. Visually, the arc appears to exist as two plasma jets extending from the electrodes with a central combined plasma region.

The vertical orientation of the plasma region creates a chimney effect that captures the injected cold reactant gases along its vertical axis. Because the plasma arc is bent at a small angle, there is a bottom region of reduced pressure that assists in effective reactant capture. The reactant gases are heated, activated, and completely decomposed in the central plasma region far from the electrode units. Since this reaction occurs at a distance from the electrode units, chemical erosion of the plasma generators is eliminated.

The ADP source has a plasma temperature of about 10,000 K and a velocity of about 10 m/sec. The plasma flow is laminar. Like a well-controlled flame, there is a central plasma region that is surrounded by a quenching or recombination zone where both physical (recombination) and chemical reactions occur . A chemical reaction zone - where activated chemical species are available for reaction - surrounds the two inner regions.

Atomic oxygen jets based on atmospheric pressure non-equilibrium plasma based on capacitive discharges [Schutze 1998] are another recent entry into plasma cleaning applications. It consists of two concentric electrodes separated by a gap of 1 to 3 mm. The inner electrode is driven with 50 to 500 W of radio frequency power at 13.56 MHz, while the outer electrode is grounded. Feed gas, containing helium and up to 5 Vol per cent of other gases, flows between the electrodes and is ionized. The gas emerges from the nozzle and impinges on a substrate placed 2 to 10 mm downstream, whereby cleaning or etching of the material takes place. The source designs are scalable to large areas and can treat a variety of objects. High-speed imaging of the plasma reveals a uniform, arc-free gas discharge.

Arc based atomic oxygen sources are also emerging as atmospheric pressure plasma cleaning applicators [Fig. 8.4]. The arc is struck between a cathode in the form of a stainless-steel disk containing a 3.175-mm-diameter circular orifice on a truncated cone at one end of a plenum through which the gas mixture flows and a tungsten needle anode inside the plenum, 1.6 mm upstream from the orifice. Inert helium is also present in the beam to keep the atoms stable until they reach the cleaning surface. The arc is powered by a 7-kVdc supply in series with a 1-MΩ current-limiting resistor. The arc is blown through the orifice, giving rise to a stream of Oxygen ions and charge-exchange neutral Oxygen atoms that are propelled about 1 cm downstream from the orifice. These Oxygen species can react with organic materials exposed to the stream.

The Measure of Cleanliness

Modern industrial practice not only demands precision cleaning, but also tests and documentation beyond subjective evaluation of cleanliness to comply with quality standards such as ISO 9000. Many quantitative techniques are available for measuring cleanliness. One such technique uses particle counters as described below.

Particle counters extract particles in a liquid medium like deionized water. A select volume is irradiated with a beam of light, usually from a laser. If there are no particles in the frame of view, the transmitted light has full intensity, while the presence of particles blocks some of the transmitted light. Appropriate electronics converts the sensed light intensity into particle size and quantity.

A simple method to evaluate the removal of organic contaminants from the metal substrates is to measure the surface tension. The surface energy of a solid can be obtained by measuring the contact angle between the surface and droplets of deionized water and precisely formulated wetting tension test solutions. The liquid interacts physically with surface contaminants and chemically with functional groups resulting in contact angle and surface energy data, which depends on the surface condition. The solutions and test methodology are in accordance with ASTM D2578-79.

When a liquid comes into contact with a solid, the liquid may wet the solid very well and thus spread across the whole surface or show less tendency to spread. This interaction between the liquid and solid is characterized by the contact angle as shown in Fig. 8.5. Contact angle measurements are based on two methodologies: static and dynamic. The static method is an optical technique based on the sessile drop method. The tangent at the solid/liquid/vapour interface is measured as a small drop of liquid is pipetted on to a surface.

The dynamic method is referred to as the Wilhelmy method [Takyi 1999]. With this method, a flat plate is held vertically on an electrobalance and a beaker of liquid is moved up (immersion) at a predetermined rate and subsequent emersion to scan the surface of the plate in order to determine the contact angle. Contact angles are measured when the stage moves up (advancing angle) and when it moves down (receding angle) and has a range from 0° (complete wetting) to 180° (complete non-wetting). The difference between the two contact angles is a property of the surfaces called the contact angle hysteresis. The lower the hysteresis the better the wettability. Hysteresis is produced by surface roughness, contamination, heterogeneity and functional group orientation. For complete wetting, hysteresis must be zero.

Electron Spectroscopy for Chemical Analysis (ESCA) can be employed to provide elemental and chemical information from the outermost 40 to 80Å of a surface. ESCA uses incident x-rays to cause photoemission of electrons from the material. The kinetic energy of the electrons emitted from the surface identifies the elements present. By measuring the exact binding energy and peak shape of a spectrum, the elemental and chemical composition of a surface can be determined. ESCA can detect both organic and inorganic surface contamination.

Cleaning of oil contamination

Stainless steel contains less than 1 percent Carbon in bulk. With the chromium oxide passivation layer at the surface, one would not expect to see Carbon as a constituent of the surface. In practice, however, metal surfaces are highly active, attracting ten to thirty atomic layers of adventitious material. This layer includes Oxygen, water, and hydrocarbons adsorbed from the ambient environment. Typical machined stainless steel surface exhibits a surface Carbon abundance of 50-100 atom percent. The top 40 to 80Å consists almost entirely of Carbon. Subsequent bonding, painting, decorating, or plating of such a contaminated steel surface would be hampered by the weak boundary layer of contamination indicated by excess Carbon [Hozbor 1994].

Cleaning rate of 2 micron/minute can be achieved by radiofrequency discharges (Korzec 1994) at the standard frequency of 13.56 MHz, with typical power inputs of 300 watts. The effective removal rate reaches the optimum value at the gas pressure of 0.2 mbar. Pressures below this limit result in insufficient chemical reactions, while higher pressures result in insufficient ion-bombardment. External magnetic field can enhance the removal rate by as much as 50 per cent for lower pressures. Here flat cathode geometries are more efficient than hollow-cathode geometries for cleaning applications.

There is a correlation with the surface temperature and cleaning efficiency and an optimum is achieved at temperatures of the order of 140° C. Both emission spectroscopy and mass spectrometry can be used for end-point detection of the cleaning process, thereby enabling the possibility of process automation for industrial systems. The cleaning rates can be increased several times by raising the applied ion energy. For example, measured oil film removal rates in low pressure (0.5 mTorr) Argon/Oxygen plasmas were raised from 0.3 µm/min to as high as 2.7 µm/min.

Cleaning for Adhesion Promotion

Bonding is a surface process and hence the properties of the surface determine the bonding strength. The adhesive has to wet the surface and spread uniformly. The key determining factor in this is the surface tension. If the surface tension of the adhesive is higher than that of the surface, the adhesive will not wet the surface. Many polymers have a low to medium surface energy (see table I). This characteristic makes it difficult to apply adhesives or coatings. Plastics with a surface energy less than 40 dyes/cm need a surface treatment before bonding.

Through the use of Oxygen plasma, one can modify the surfaces of these materials such that they obtain the best possible contact with the adhesive or coating. For example plasma processing can increase the surface energy of polypropylene from 29 to 72 dynes/cm, which is approximately the value for full water contact.

There has been some concern that samples may be damaged in an RF field or in aggressive plasma. The evidence of damage is not conclusive and seems to occur only under very high RF power for repeated and extended periods of up to 60-120 minutes.

Applications in Semiconductor Processing

Semiconductor processing industry uses plasma chemical vapour deposition and etching extensively. Commonly deposited CVD films include polycrystalline silicon, silicon nitride, silicon dioxide, and metals such as Tungsten. The microscopic transistors and circuit components are interconnected using tiny wires of conducting material deposited on the insulated layers.

The remnants of the CVD process get coated on internal walls of the CVD reactor. But the risk here is that these deposits would peel of and contaminate the subsequent process cycle. Plasma cleaning of inner wall of the CVD chamber after the deposition is thus an essential step to maintain the production yield [Maroulis 1994]. Traditional cleaning agents are gases such as PFCs and SF_6, which contain Fluorine. These are used as plasma cleaning gases for removing the SiO_2or Si_3N_4 deposited on the inner walls of CVD chambers. During the clean cycle, the FFC is converted to F atoms in a plasma, which chemically etches away residual material from chamber walls, electrodes, and chamber hardware.

It takes a lot of energy to dissociate FFCs. Hence a substantial fraction of the gas flowing into the chamber during the cleaning process is not dissociated into F-atoms. The unreacted gas is exhausted from the chamber and, unless emission abatement technologies are used, they flow eventually into the atmosphere. These gases have large global warming potentials (GWP), four orders higher than that of CO_2, and very long lifetime in the atmosphere. The efforts to develop the technology for the gas emission suppression started circa 1994 [Sematech]. NF_3 has been regarded as a gas for which a new gas with small GWP value should be substituted.

Another manufacturing step used in the semiconductor industry is the definition of the circuit element on the silicon wafer using photosensitive organic materials called photoresists. After use, however, the photoresist must be completely removed by etching before starting the deposition process. Conventional cleaning technique employed hot solutions of sulfuric acid with hydrogen peroxide as well as toxic organic solvents. However, plasma etching using gases such as sulfur trioxide helps in reducing the volumes of wet chemicals and organic solvents. It has been documented that the reduction of wet chemical usage can be as high as 1000 times and that savings in commercial cost alone can be of the order of $ 300,000 each month from a typical manufacturing fab.

Cleaning Spacecrafts for Planetary Missions

Planetary missions like the Mission to Mars demand unbelievably high standards of cleanliness of the spacecraft and the payloads. The planet too has to be protected from contamination transported form the earth. The scientific objectives of the mission- for example the search for Martian life forms- will be compromised if organic matter makes the trip as stow away [Orgel 2000]. The prescribed contamination limit for surface carbon is less than 10^{15} atoms/cm^2, which can be reached only by plasma and CO_2 snow cleaning techniques. Of these, plasma cleaning has been found superior in cleaning mill-finished surfaces [Mickelson 2002].

Applications in Marking/Printing

Paint adheres well with a clean surface. A 10 nanometer surface film can weaken coating adhesion [Mittal 1995]. Surface organics and oxides have caused problems in marking packages for years. With the introduction of new ink compositions and new packaging materials, marking permanency is becoming a more wide spread problem. Until recently, the most common means of addressing this had been wet cleaning. However, this process requires submersion of an entire package. The high pH factors that are often found in these wet chemicals discolour leads and other metallic surfaces besides attacking ceramic substrates. Other means of addressing this problem have been flame, UV, and corona discharge. These processes offer limited life, limited throughput, presents employee safety issues, and in some cases, causes package damage.

In the last few years, many number of companies have turned to plasma as an effective, safe, and efficient means of removing oxides and organics from both metal and polymer surfaces. Different substrates require different processes and the measurement of these results is often subjective. One means of measuring surface modification is surface energy.

Sterilisation and Deodorization of Food Containers

Plasma chemical reactions such as etching and oxidation processes, electron bombardment, UV irradiation and surface ablation can destroy micro-organisms through creating damage in the cell membrane, destroying its DNA and proteins.

The efficiency of plasma chemical reactions depends on the chemical composition of the plasma and the specific energy input. The characteristic energy of plasma particles generally is much higher than the binding energy of the organic molecules in the microorganism. Electron bombardment is important if the microorganisms are lying on a surface or suspended in a volume and is crossed by the electrical current generated in the plasma. The efficiency of this process will depend on the current density and the electric fields in the plasma. UV irradiation depends on the radiation density and is determined by the processes of plasma generation and decay. Ablation is a hydrodynamic phenomenon accompanying any intense dense plasma treatment of the surface.

Geometry determines the acceptable type of plasma sources for application like large-scale destruction of microorganism inside food containers [Koulik]. The RF flash discharge has been used to generate the plasma inside the containers. Here the electrode geometry consists of a central electrode located outside the bottle above its neck and a second, external grounded electrode surrounding the bottle. Diagnostics based on light emission show that the plasma is generated at the axis of the bottle and propagates to the wall and then vanishes in the reverse sequence.

Spores (Bacillus subtilis), yeast (saccharomyces cerevisiae), molds (aspergillus niger) resident on the inner surface of the bottles have been destroyed by short duration treatments. The main tests were made with Byssochlamys nivea, a microorganism characteristic for beverages. This micro-organism has been found to be stable in acid liquids (pH<5) and at temperatures upto 98◦ C.

Biological Decontamination

Global terrorism and the apprehension of terrorist attacks using biological weapons have spurred research on using plasma streams from atmospheric pressure plasma devices for decontamination of bacterial agents. The atmospheric pressure plasma jet (APPJ) developed at the Los Alamos National Laboratory [Hermann 1999] has been successfully deployed to counteract this problem. This device contains two coaxial cylinders excited by radio frequency voltage and converts a gas flowing through the annular gap into plasma. The plasma contains metastable molecules of Oxygen, Sulphur and Hydroxyl radicals, which are highly reactive and have sufficiently long lifetime to be useful for decontamination applications.

The typical decontamination process for an exposure to chemical or biological agent involves large amounts of highly corrosive substances and usually takes 30 minutes to be effective. APPJ has been tested for the destruction of Bacillus globigii, similar to the Bacillus anthracis, which causes anthrax, resulting in the destruction of 10 million spores of bacteria in 30 seconds. APPJ has also been tested on 2-chloroethyl phenyl sulfide, a chemical with composition similar to the mustard gas [Frazer 1999]. Tests against the VX nerve gas agent, which is apparently in the stockpile of many nations, are being contemplated. The US department of defence is conceptualising a walk-through plasma shower for treatment of contaminated persons; similar to the Clorox chemical shower that is used at present for decontamination.

Plasma Cleaning of Paintings

Paintings, sculptures and other great works of art are vulnerable to ageing, fire and vandalism. Natural resins, which constitute the varnish used as a protective layer on paintings, darkens and crack with age. Several paintings are damaged by the soot deposited by smoke. Traditional solvents such as acetone or alcohol used to remove the surface smear may actually attack the paint irreversibly - a case of cure being worse than the disease.

In a classic example of spin-off from space programme being put to earth based applications, NASA [1996] has reported a number of studies on the use of monatomic Oxygen to remove undesired organic materials from the surfaces of paintings [Fig. 8.7]. Spacecrafts use a variety of polymers. These materials disintegrate into carbon monoxide and carbon dioxide gases, due to the interaction of the copious amounts of photo-dissociated atomic Oxygen in the space environment. Earth based facilities that produce atomic Oxygen for material exposure is used in studies designed to mitigate this problem.

Atomic oxygen reacts with carbonaceous deposits on the surfaces of paintings, converting the Carbon to CO and CO_2 and converting any Hydrogen content of the deposit to H_2O vapour. The use of monatomic Oxygen enables the removal of carbonaceous deposits at controlled rates, and cleaning can be stopped at any point.

A painting to be cleaned is typically placed about 8 mm downstream from the orifice. Because the spot that is cleaned by exposure to the stream is only 3 to 5 mm wide, it is necessary to translate the apparatus gradually along the painting surface to clean a larger area. The apparatus was used to clean lipstick defacement from an Andy Warhol painting vintage piece, ‘Bath Tub’. Monet’s water lilies, which were charred in a New York gallery in 1958, and possibly the removal of soot off ancient Egyptian paintings that were scorched by candle flames of past squatters, are also possible future projects.

Plasma-chemical Treatment of Archeological Artifacts

Plasmachemical treatment of archaeological artifacts is a relatively new technique developed during the 1980s [Veprek 1985]. Although this technique has been used for conservation of artifacts whose components are mainly metals, the plasmachemical process as such has been used more or less intuitively. The process is based on using low-pressure Hydrogen plasma in which the artifacts are treated for several hours, usually in several steps. The problem is to determine the optimal period of the plasma treatment and to characterize its efficiency. The ancient artifacts always contain some corrosion layers on their surface. Studies focused on the composition of the layers show that various oxide and chloride complexes, usually containing crystalline water too, are the dominant compounds of the layer. Naturally, the actual composition of the corrosion strongly depends on the matter surrounding the artifact before the discovery.

The principle of plasmachemical treatment is based on removal of the oxide and chloride molecules in low-temperature low-pressure Hydrogen plasma produced by capacitively coupled RF discharge. The process usually takes place at total gas pressure of 100 Pa and hydrogen flow rate of 100 Sccm.

Economics

Compared to liquid cleaning systems, plasma is considerably less expensive when all costs of chemical storage, disposal, and liability are factored in. After an initial capital purchase of $60K for a medium-sized plasma system, operating costs are minimal.

For example, one tank of industrial-grade oxygen gas (about $20) will often last a year or more for light cleaning. Comparable liquid cleaning processes typically require gallons of solvents or aqueous cleaners costing at least hundreds of dollars a month plus disposal expense up to $500 per drum, not including permits. Additional savings will be realised as operators spend less time on chemical monitoring and safety systems.

Training time is also minimised with dry processing since commercial plasma cleaning reactors are well instrumented. After loading parts into the reactor, one button activates the system to carry out each step of a pre-programmed process. Fail-safe shut-off controls automatically stop the process if some part of the system falls outside of preset operating specifications. Moreover, operators usually are able to carry out other tasks while parts are being cleaned.

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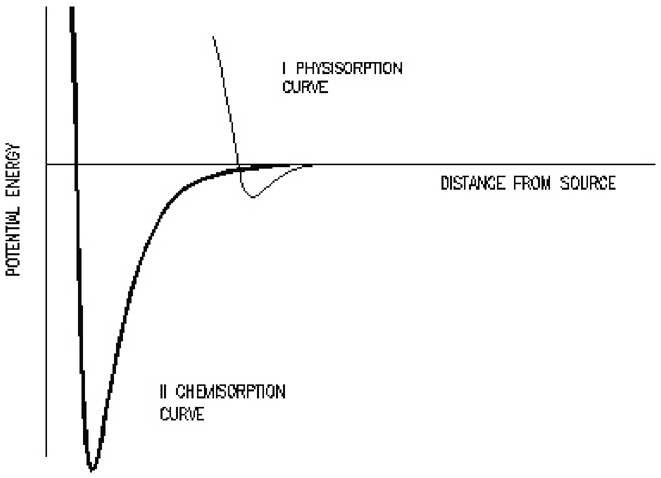
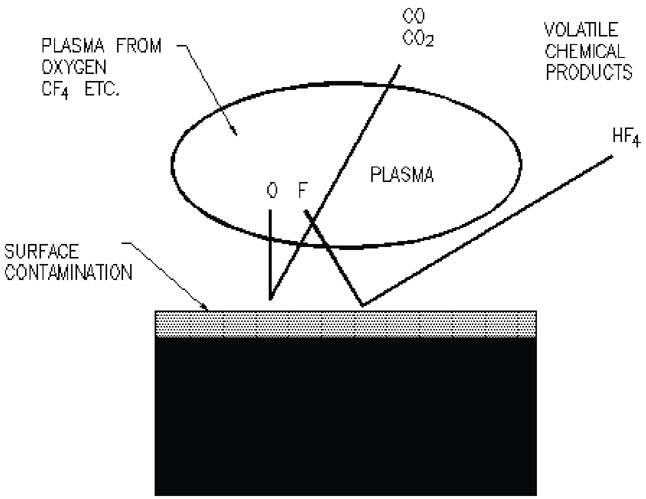
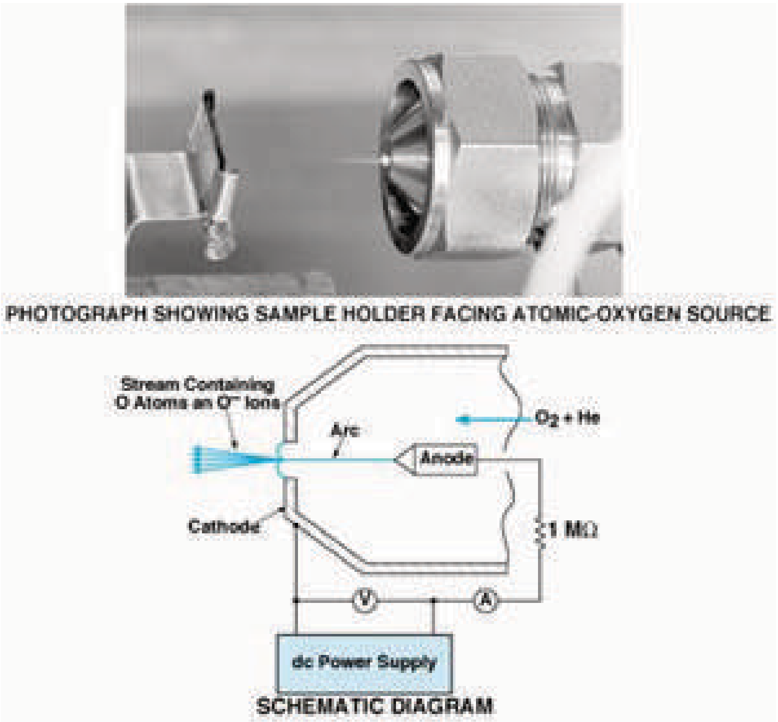


Fig. 8.1. Physical and chemical basis for surface contamination



es is based on the chemical reaction and volatilisation of surface contaminants by plasma species.

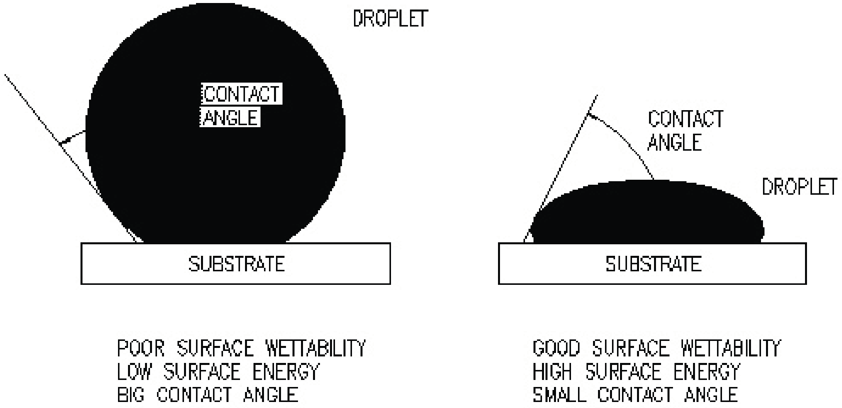


hotograph

Plasma Etch, Inc.

PE-200® Research & Development Series, Small footprint, excellent results! Fast, Reliable and Affordable. The PE-200® features touch--screen controls with a Windows®-based operating program. Beginning at $38,000.00 complete with vacuum pump.

Fig. 8.3. Photograph of a commercial plasma cleaning system (Photo courtesy of PlasmaEtch Systems Inc.)



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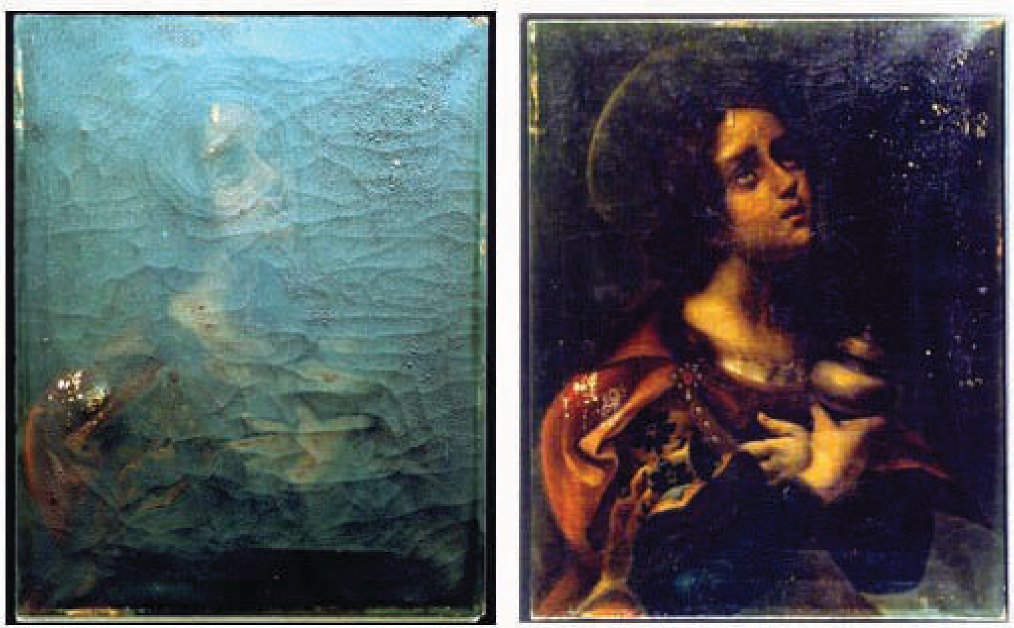
surface is a measure of the surface energy



a plasma source (photo courtesy of NASA, USA)

9. Biomaterials and Plasmas

Surface Modification of Polymeric materials

Materials used in biomedical applications have to be biocompatible and even bio-interactive. Various plasma techniques have been developed to render such properties to materials used in biomedical applications. This chapter will review these techniques and indicate applications, which have become important to modern medical practice.

Materials for Biomedical Applications

Materials for biomedical applications – biomaterials – are those, which are used to replace or restore function of a body part [Fig. 9.1] and are in intermittent or continuous contact with body fluids for short or long time spans [Park 1984]. Biomaterials can be natural or synthetic and are used in the fabrication of orthopaedic, cardiovascular, neurological, dental, drug delivery and other applications [Hill 1998]. Orthopaedic implants are used both as fracture fixation devices and as artificial joints. The materials used include Aluminium, Cobalt Chromium alloys, stainless steel, Titanium alloys, Teflon and polyethylene. 138,000 hip joints and 245,000 knee prostheses were implanted in the US in 1996 [Praemer 1999]. Moreover, the annual world markets for prosthetic heart valves is of the order of 260,000. Hence biomaterial surfaces are considered in biomedical industry to be among the most critical areas of concern and opportunity in the biomedical industry [OST 1995].

Materials such as plastics, polymers, resins, ceramics, reconstituted or specially treated natural tissues, composites and synthetic biomaterials have properties that lend themselves well to the manufacture of medical appliances or devices [Blanchard 1995]. Polymeric biomaterials include fibres, rubbers, moulded plastics, emulsion, powders, coatings and fluids. Hydrogels such as poly vinyl alcohol (PVA) and polyethylene glycol (PEG) are structures that form a hydrophilic cross-linked network which swell with absorption of water. Significant biomaterials and their properties and applications are listed in table I. Biomaterials are relatively inexpensive and can be easily moulded into complex shapes. Their bulk physical properties may be selected from a wide range of parameters such as rigidity and temperature stability.

Synthetic polymers are used in implants and devices intended to work in contact with human blood in short, medium and long term. Vascular prostheses are made of Dacron (plyethelyne thereptalate) and Goretex (expanded polytetra fluoroethylene). Blood bags are made of polyvinyl chloride with a plasticizer. Membranes for haemodyalisis are fabricated with polypropylene. Heart valves made from polymers that are coated with pyrolytic carbon [Favia 1998].

A generic property demanded of all biomaterials is that they be biocompatible or recently even bioactive. Aspects of this in terms of interaction of these materials with human tissues are illustrated in Fig. 9.2. Ideally, biocompatible materials should minimally disrupt normal body functions. They have to perform in the aggressive environment of the body permeated by fluids, which have a pH of 1-9 [Ramakrishnan 2001]. Adverse physiological reactions such as thrombosis formation, toxicity, allergic inflammation and infection can result in the absence of biocompatibility. Bioactive materials can actively promote benign interaction between such materials and the surrounding tissue, as illustrated in Fig. 9.3. Medical procedures in current practice, which are mostly based on inert biocompatible materials, are beginning to look favourably at bioactive materials. All these properties will determine whether the foreign object implanted into the human body would be accepted or rejected. Biological interface reactions within the body or in the laboratory can limit their in vivo and in vitro performance.

The past decade has witnessed a surge in interest in various physical and chemical techniques for modification of surface properties to improve their biological response to blood or tissue fluids [Katz 1997]. These technologies make it possible to change the surface properties of a material without changing the bulk properties. This essentially creates "new" materials with new possibilities, opening up novel prospects to help resolve design and manufacturing issues and develop innovative applications. Manufacturing difficulties frequently arise when a new material substituted for an existing one exhibits surface characteristics that are incompatible with effective processing. New surface modification methods often can address such problems while also revealing new design solutions as designers begin to think beyond conventional mechanical or chemical surface alteration.

Plasmas and Polymer Surfaces

Low-pressure plasma technology provides an environmentally friendly and economic way to modify material surfaces on a microscopic level without resorting to mechanical operations or using chemicals [Sheu 1995]. With this technique, it is possible to clean, activate, etch, or otherwise modify the surface of plastic, metal, or ceramic materials to improve their bonding capabilities or achieve totally new surface properties. Potential medical applications include modifications of hydrophilic, hydrophobic, low-friction, and barrier surface characteristics. Various surface modification techniques are being investigated to control tissue adhesion, reduce tissue drag, provide thromboresistance or infection resistance and act as immobilisation agents for chemotherapy and removal of particular protein cells. The primary focus is on the surface properties that could affect tissue reactions over short and long periods of time.

Plasma technology offers a technique for altering just the first few atomic layers for rendering the surfaces of most medical polymers wettable so that adhesive bonding can be achieved to materials such as polyolefins, silicones, and fluoropolymers. In a similar fashion, more exotic processes such as plasma grafting, and polymerisation can produce totally new custom surfaces without loss of the desirable characteristics of the bulk material. Plasma treatment does not affect the bulk properties of materials and plasma treated parts are generally visually and physically indistinguishable from untreated parts. Plasma processes are now routinely used for controlling the wettability of test tubes and lab vessels, for pre-bonding preparation of angioplasty balloons and catheters, for treating blood filtration membranes, and to manipulate surface conditions of in vitro structures to enhance or inhibit culture cell growth.

Plasma treatment usually refers to a plasma reaction that either results in modification of the molecular structure of the surface or atomic substitution [Hollohan 1974]. Even with benign gases such as Oxygen or Nitrogen, plasma treatment can create highly reactive species at low temperatures. Energetic ultraviolet light is emitted in the process, which along with the fast ions and electrons provide the energy necessary to fracture polymer bonds and initiate chemical reactions at the surface. Only a few atomic layers on the surface are involved in the process, so the bulk properties of the polymer remain unaltered by the chemistry, while the low process temperature eliminates concerns about thermal modification or distortion of the bulk. Unique reactions can be promoted by appropriate choice of reactant gases and process parameters and unusual polymer by-products and structures can be formed. It is frequently possible to select reactants that form volatile by-products upon reaction of the plasma with the substrate material. These, upon desorption from the surface of the treated material, are removed by the vacuum pump, resulting in etching of the surface without the necessity for further scrubbing or neutralising.

Plasma Surface Modification Processes

The process of plasma surface modification on polymer, fluoropolymer, and other plastic surfaces can be divided into four distinct mechanisms: ablation, cross-linking, activation, and deposition [Fig. 9.3].

Ablation is the process of breaking down weak covalent bonds in a polymer through bombardment with high-energy particles. This affects the outermost molecular layers of the substrate exposed to the plasma, which boils off and is removed by pumping. Because the chemistry of any layers of surface contamination is also generally made up of weak C-H bonds, plasma treatment can remove contaminants such as oil films or injection moulding additives, thereby leaving behind a uniformly clean and active polymer surface.

Cross-linking sets up of chemical links between the molecular chains of polymers. Processing with inert gases can be used to cross-link polymers and produce a harder surface with improved wear or chemical resistance. Medical devices, which benefit from plasma-induced cross-linking, include catheters, clinical instruments, and contact lenses. This chemistry may also be used to partially substitute Hydrogen atoms for Fluorine or Oxygen in polymer surfaces. The noble gas species, such as Argon or Helium, are chemically inert, so they do not combine or become part of the surface chemistry. Instead, they transport energy to break chemical bonds in polymer chains. Broken polymer chains result in "dangling bonds," which recombine with other reactive sites, resulting in significant molecular restructuring and cross-linking. The creation of dangling bonds allows for chemical "grafting" reactions to occur. This process is involved in several of the biomedical applications.

Activation is the process of replacement of surface polymer groups with chemical groups from the plasma. The plasma breaks down weak bonds in the polymer and replaces them with highly reactive carbonyl, carboxyl, and hydroxyl groups. Activation can also be performed with amino groups or other functional groups. The type of chemical groups incorporated into the surface will determine the resulting change in substrate characteristics. Active groups on the surface can change the surface characteristics, such as its wetting properties, adhesivity, etc.

Plasma polymerisation is the process of forming very large molecules by the joining of many small linkable molecules called monomers [Ratner 1990]. The processes involve reactions utilising a wide variety of gases, organic or organo-metallic vapours, which deposit non-volatile polymer films. The monomer is decomposed and excited and fragments form new molecules in the gas phase or on the surface. The active species move to the surface where they are desorbed into the gas phase. Each sorption represents a deposition step. The sorbed molecules subsequently interact and engage in ionic or radical polymerisation on the surface and thus form a thin film. And even s the film is being formed, the newly created surface atoms and molecules are subjected to the bombardment by the species from the gas phase and the electromagnetic radiation from the plasma. Classical polymers have reactive structures such as double bonds that allow them to bond to one another. The double bond in methyl methacrylate providing the linking site for forming polymethyl methacrylate is an example of a known polymerizable molecule forming a polymer under plasma conditions.

Plasma can also polymerise materials, which do not normally form polymers under the conventional chemical methods. Plasmas can fractionate gases that lack linkable sites into many new and reactive compounds that subsequently may polymerise. In the deposition of aliphatic and aromatic polymer films in a plasma, all monomers, saturated or unsaturated can be made to polymerise, including those that are not polymerised by any of the conventional techniques. Due to the physical and chemical complexity of the process and its strong relationship to process parameters the film properties can be controlled during deposition and combine different features such as good adhesion of the film at the substrate surface and high hardness at the upper film surface.

Plasma Processing of Medical Devices

The strong interfacial forces manifested in chemical compatibility or bonding promotes adhesion between two surfaces [Liston 1989]. Polymers generally have low to medium surface energy and adhesives or coatings do not stick to such surfaces. Oxygen plasma processing can increase the surface energy of polypropylene from 29 to 72 dynes/cm, which is approximately the value for full water contact. Other surface activation processes make them nitrated, aminated, or fluorinated. Plasma surface modification can help form functional groups such as amine, carbonyl, hydroxyl and carboxyl groups, which improve interfacial adhesion [Hook 1987]. Adhesive bonding of catheters and balloon catheters, dialysis filters and other components, and bonding needles to syringe hubs and plastic film for blood and drug bags have benefited from plasma activation processes.

Conventional cleaning methods are imperfect and usually leave a thin contamination layer. In the same way that weak chemical bonds are removed in the activation process, contamination layers can be eliminated even from the most of surfaces. Plasma will remove oil films, microscopic rust, or other contaminants that typically form on surfaces as a result of storage or previous manufacturing processes by chemically converting them into high vapour pressure volatile gases [Loh 1999]. Injection moulding additives, silicone-based compounds, release agents, and partially absorbed contaminants can be efficiently removed from plastics, metals, and ceramics. Plastic additives capable of interfering with subsequent manufacturing can be eliminated by plasma without destroying or changing bulk substrate properties. Extremely sensitive instrumentation parts or implants can be cleaned via plasma processing.

Plasma wetting has been used to decrease the contact angle of various liquids including water on a large variety of substrates. Contact angles as low as two degrees have been demonstrated after only few minutes of plasma treatment. Permanent hydrophilicity can be imparted to woven or nonwoven textiles used as blood filters or filtering membranes for various applications, including microfiltration components for dialysis filter systems. The surfaces of cell culture substrates, such as Petri dishes, Roller bottles, microcarriers and membranes, can be modified by plasma to greatly increase wetting. This improves cell growth, protein binding and cell-specific attachment by controlling surface chemical structures, surface energies and surface charge states

It is possible to plasma polymerise the surface of nonwovens and other textiles so that they become hydrophobic. Hydrophobic surfaces repel water, so that when submerged in aqueous solutions, they no longer draw fluid by capillary action. Applications include oleophobic or hydrophobic treatment of paper, textiles, and filter elements. Fluorinated species such as Tetrofluoromethane, Sulphur Hexafluouride and perfluorohydrocarbons may be used to induce substitution of Fluorine atoms for Hydrogen atoms in the surface structure. Teflon-like structures may be created, resulting in a very hydrophobic, chemically inert surface with high chemical stability.

The activation of surfaces to promote cell growth or protein bonding to decrease thrombogenicity is another important application [Favia 1998]. Fluorinated Teflon-like coatings and silicone-like coatings deposited from organosilicon monomers are blood compatible. The ratio of Fluorine and Carbon in the film (F/C ratio), its wettability and morphology are apparently related to the absorption and retention of fibrinogen, a protein in the human blood involved in the coagulation process [Favia 1996]. Teflon like films with different morphology can be prepared with PECVD.

Silicone-like films are obtained by plasma polymerization of silicon containing organic monomers. Deposits of $Si_xC_yH_kO_z$ compositions have been utilized to coat active Carbon particles in blood filters and PP hollow fibre membranes [Hasirei 1986]. Haemoperfusion is a process where blood is detoxified by circulation through columns filled with sorbents such as activated Carbon, enzymes, antigens, antibodies etc. Carbon granules have to be coated with polymer films to inhibit fine Carbon particle release into the blood. Similarly, micro porous polypropylene blood oxygenators are coated with thin silicon-like polymeric film to reduce blood cell damage by micro roughness of the membrane surface [Piskin 1992].

It is known that heparin and heparin-like molecules, collagen, albumin and other molecules of biological origin confer anti-thrombotic properties on polymer surfaces where they are immobilized. Therefore, polymers are activated and made to react with the molecules to be coupled. Empirical approaches prevail in this process. Most frequently grafted molecules are $–NH_2$, -OH and –COOH using non-depositing feed such as NH_3, O_2, H_2O etc. [Gombotz 1987]

Amine functional groups attached by ammonia plasma treatment acts as attachment sites for anticoagulants such as heparin [Yuan 1993]. Examples of in-vitro uses include preparation of petri dishes and micro titre plates for laboratory experiments or for drug manufacturing. The process can also be used to enhance the biocompatibility of implants such as vascular grafts [Kiaei 1988], lenses, and drug-delivery implants, by treating the surface of a device to increase the adherence of a hemocompatible coating. When required, surfaces can also be modified to decrease the bonding of proteins or cells for applications involving contact lenses and intraocular lenses [Brinen 1991].

Many materials encourage protein binding and thus initiate clot formation. Thrombogenesis, the propensity of a surface to form or initiate clotting is reduced by anticlotting coatings applied to the surface [Bauser 1984]. Antithrombonin coatings often fail to effectively bond to the polymer surface. Using active gas plasma, surfaces may be modified by heparinizing or by grafting of antithrombotic functional groups, which enhance effective chemical bonding. Process variables are dependent upon a range of factors including selection of the base materials, composition of the antithrombotic, and the expected product lifetime. Animal test results of the surface modified and heparin coated polyurethane catheters revealed no protein attachment after a 30-day contact. Testing on surface-modified but uncoated polyurethane catheters exhibited only slight protein attachment, while unmodified catheters show severe thrombus formation. Tests performed on modified blood filters showed substantial reduction in platelet retention, in comparison with untreated materials.

It is sometimes necessary to manipulate surface conditions of in-vitro structures so as to encourage or enhance culture cell growth. In specific cases where cell attachment is necessary to ensure proliferation, plasma modified in-vitro culture cell containers yielded dramatic improvement over untreated containers. Testing has confirmed that, by using gas plasma surface modification procedures, materials such as PET, polyethylene and K-Resin can yield substantially higher performance than in the untreated state.

Some silicones and polymers such as polyurethanes have a high coefficient of friction against other surfaces. By plasma treating components made of such materials, a polymer coating with a lower coefficient of friction can be applied to create a more lubricious surface. For example, plasma surface modification can improve the adhesion of hydrogel coatings on catheters, which can reduce friction between catheters and the walls of blood vessels. The instruments used for catheterization in urinary, tracheal and cardiovascular tracts or for endoscopy/laparoscopy procedures as well as the ophthalmologic materials should have a surface, that preferably, becomes slippery upon contact with aqueous body liquids. Gas plasma can create such a low friction surface that would enable easy insertion and removal from a patient's body and will prevent mechanical injury to the mucous membranes and minimise discomfort to the patient. Gas plasma has been used successfully, either by itself or in combination with other techniques, especially the Xylylene polymerisation, in manufacturing of medical instruments used for various procedures, such as ophthalmology and videosurgery.

Barrier coatings with reduced permeability of plastic parts to alcohol or other liquids or vapours can be deposited by thin film deposition. For example, plasma treatment of high-density polyethylene can decrease the material's permeability to alcohol by a factor of 10. Current biomaterials such as silicon rubber, polyester, poly-tetrafluoroethylene, polyurethane and PVC can be used only for limited duration as blood contacting implants because of blood-biomaterial interaction which causes blood coagulation. For instance, in PVC blood bags, Dioctyl Phthalate (DOP) and certain stabilisers slowly migrate from the PVC matrix to the surface and interact with the blood, which results in clotting of the blood. Plasma treatment of known controlled delivery systems can overcome both problems by creating a tightly cross-linked barrier membrane, which is biocompatible and regulates the dispersion rate within a narrow range.

Membrane materials can also be modified to enhance the diffusion selectivity. Normally, membrane material should exhibit high selectivity to permeation while retaining high permeation rates. Incorporating chemical functionality or physical restrictions to control pore size can enhance selectivity. Haemodyalis, protein purification etc. are such bio-separation processes which can benefit from this process [Poncin-Epaillard 1992]

Diagnostic Biosensors normally require the immobilisation of a biological component such as enzyme or antibody onto the sensor surface. Surface grafting and functionalization offers a convenient and efficient way to establish covalent bonding between the biological component and the support matrix.

Plasma Sterilisation

A basic requirement for all biomaterials, which are implanted into the body, is that they be sterile. Sterilisation is the process of destruction of infectious agents by a suitable physical or chemical means. The effectiveness of sterilisation is quantitatively represented by the sterility assurance limit (SAL). An accepted minimum value of SAL is 10^{-6}, implying that only one part in one million devices may fail [Ratner 1996].

Conventional methods of sterilisation involve the destruction of bacteria by heat, chemical agents or radiation.   The autoclave uses steam under pressure   at temperatures of at least 120 degrees for 30 minutes or longer. Polymeric materials presently used widely in medical and surgical appliance undergo severe chemical or morphological changes when subjected to high temperature sterilisation [Athanasiou 1996]. In fact, the utility of the material can be destroyed due to the alteration in bulk, interfacial or surface properties.

Many chemical agents exhibit disinfecting properties. In the late 1950s, hospitals began using ethylene oxide (EtO) as a low-temperature method to sterilise medical and surgical instruments. EtO destroys microorganisms by alkylating the amine groups in nucleic acids [Ratner 1996]. EtO is both toxic and a recognised carcinogen, requiring hospitals to install expensive monitoring, abatement, and aeration equipment besides providing protective clothing and safety training for workers. Parts sterilised by Ethylene oxide have to be washed in air for long periods after sterilisation to remove residues forcing hospitals to maintain large and expensive equipment inventories to accommodate sterilisation cycle time. Finally, because it is explosive, EtO is often mixed with flame-retardant carrier gases such as CO_2 or Freon. Despite these drawbacks, until recently there was no available alternative low-temperature sterilisation process.

In the early 1970s, radioactive cobalt emitting gamma rays became available at reasonable price and quantities, which prompted the development of ionising radiation as a simple and effective sterilising agent. Gamma rays transfer energy to the materials by Compton scattering collisions with atomic electrons. The result of this interaction is that the electron recoils a short distance as an unbound electron giving up its energy to the atomic structure of the material by ionisation and free radical formation, while the scattered gamma ray carries the balance of energy as it moves through the material. Gamma radiation from radioactive cobalt destroys the nucleic acids of the contaminating microorganism [Ratner 1996]. By the early 1980s, gamma radiation from cobalt had become a serious alternative to EtO fumigant. Because the probability of Compton scattering is relatively low, the gamma rays will penetrate deep into the material. This means large volumes will be treated at low dose rates.

Gamma radiation can cause degradation of polymers by chain scission resulting in cross-linking within many polymers [Costa 1998]. Gamma radiation at prescribed dosages below the limit for crosslinking of polymers takes too long a time for sterilisation. An operational problem with gamma ray sterilisation is the strict protocols relevant to the use of radioactive materials, which have to be put into place and conformed to by establishments

Ionising radiation can be delivered by means other than those using radioactive sources. Machine generated X- rays from intense electron beams has been used for sterilisation in parallel with gamma sterilisation. The cross section for electro-electron and electron-nuclear scattering is much higher than for Compton scattering. Hence electrons of say 10 MeV energy will penetrate only about 5 cm into the material while the ^{60}Co gamma radiation will penetrate 50 cm into the material.

Gas plasmas are increasingly being employed to sterilise the surfaces of medical components or devices. The disinfecting and sterilising properties of the plasma environment have potential for applications in biomaterial device fabrication and surgery. It is less capital intensive than electron-beam sterilisation; it is less toxic than ethylene oxide sterilisation and since it operates at ambient temperatures is less prone to thermal and hydrolytic attack than steam sterilisation. For example, it is well suited to materials that are sensitive to heat or radiation. It can be more time and cost effective compared to the conventional techniques and it can be used to sterilise pre-packaged articles and eliminate the aeration time necessary in some chemical sterilisation techniques.

Menashi described a surface plasma sterilisation scheme in a 1968 patent assigned to the Arthur D. Little Co. [Menashi 1968]. Further developments were due to Menashi and Ashman, Boucher, Bithell, Mcgowan [Ashman 1972]. In 1987, a patent was issued to Surgikos, Inc, a Johnson & Johnson Company, disclosing the use of hydrogen peroxide plasma [Jacobs 1987]. In another patent issued in 1988, the ability of low temperature plasmas to remove traces of residual hydrogen peroxide from medical materials was claimed [Jacobs 1988]. The importance of these two critical features in plasma based medical sterilization has been discussed by Addy [1989]. The production of highly reactive radicals and ions in a plasma discharge is most important in sterilisation. The sporicidal action of the plasma is not greatly affected by the presence or absence of ultraviolet radiation in the hydrogen peroxide plasma. However, sterilization by N_2 and O_2 plasma is considered to be primarily due to UV radiation from the discharge [Soloshenko et. al 2000]

Tegal Corporation, an American company is already marketing RF glow discharge plasma systems for a variety of biological surface cleaning applications, including sterilisation. The pre-treatment of tissue culture substrates in the laboratory via an inert gas glow discharge has demonstrated a vast improvement in the tissue cell attachment to the surface, providing a more reliable cell-substrate interface while doubling the cell plating efficiency. Sterilisation is also adequately accomplished during the treatment process

In 1993, Advanced Sterilisation Products (ASP), a division of Johnson & Johnson Medical, Inc., introduced the patented STERRAD® Sterilisation System [Fig. 9.4]. The low-temperature hydrogen peroxide gas plasma in the STERRAD System effectively sterilises medical and surgical instruments, overcoming the heat and moisture limitations of steam and the toxicity of EtO [Jacobs 1987]. In August 1997, recognising the broader potential of the STERRAD System, the Food and Drug Administration (FDA) cleared the sterilizer system for expanded use with an even larger number of medical and surgical instruments, effectively enabling it to operate as the sole sterilisation system for many healthcare facilities. The STERRAD process cycle uses a 59 per cent aqueous solution of hydrogen peroxide vaporized in a vacuum chamber and converted into plasma using RF excitation. The plasma produced in annular region between a mesh electrode and the vacuum chamber wall creates OH radicals, which diffuse into the central region, uniformly bathing the material to be sterilised. This is illustrated in Fig.9.5. The reactive species formed due to the dissociation of hydrogen peroxide are capable of killing microorganisms.

The two viruses tested, poliovirus type I and herpes simplex virus type I are representative of the two major classes of viruses, hydrophilic and lipophilic respectively [Jacobs 2001]. Of these, the hydrophilic group normally exhibits the largest resistance to chemical sterilants. The STERRAD process has demonstrated virus destruction efficiency in both cases.

Highly effective sterilisation technology is especially important given growing concerns about the increasing prevalence of previously rare or newly discovered viruses and bacteria and the challenge they represent to nosocomial infection control. Many hospitals are abandoning EtO-based systems in favour of newer low-temperature sterilisation technologies such as the STERRAD System, which is faster, more cost effective and safer for workers, patients, and the environment than EtO and other low-temperature sterilisation technologies. The STERRAD System can sterilise nearly all medical devices, unlike other newer low-temperature sterilisation alternatives that can only sterilise selected instruments.

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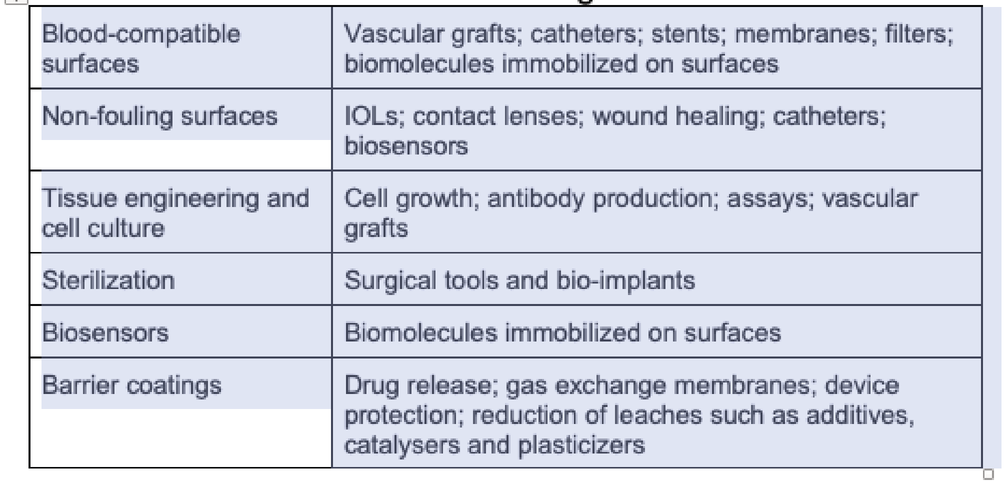
Table I: Biomaterial Processing



Blood-compatible surfaces	Vascular grafts; catheters; stents; membranes; filters; biomolecules immobilized on surfaces
Non-fouling surfaces	IOLs; contact lenses; wound healing; catheters; biosensors
Tissue engineering and cell culture	Cell growth; antibody production; assays; vascular grafts
Sterilization	Surgical tools and bio-implants
Biosensors	Biomolecules immobilized on surfaces
Barrier coatings	Drug release; gas exchange membranes; device protection; reduction of leaches such as additives, catalysers and plasticizers

Table I. Typical material surface-tension and contact-angle values.

Materials	Surface Energy (dynes/cm)		Water Contact Angle (degrees)	
	before	*after*	*before*	*after*
Hydrocarbons				
Polypropylene	29	>73	87	22
Polyethylene	31	>73	87	42
Polystyrene	38	>73	72.5	15
ABS	35	>73	82	26
Polyamide/polyethylene copolymer	<36	>73	63	17
Epoxy	<36	>73	59	12.5
Polyester	41	>73	71	18
Rigid PVC	39	>73	90	35
Phenolic	None	>73	59	36.5
Fluorocarbons				
PTFE polyethylene copolymer	37	>73	92	53
Fluorinated ethylene propylene	22	72	96	68
Polyvinylidene	25	>73	78.5	36
Elastomers				
Silicone	24	>73	96	53
Natural rubber	24	>73	None	None
Latex	None	>73	None	None
Polyurethane	None	>73	None	None
Styrene	48	>73	None	None
Engineering thermoplastics				
PET	41	>73	76.5	17.5
Polycarbonate	46	>73	75	33
Polyamide	40	>73	79	30
Polyaramid	None	>73	None	None
Polyaryl ether ketone	<36	>73	92.5	3.5
Polyacetal	<36	>73	None	None
Polyphenylene oxide	47	>73	75	38
PBT	32	>73	None	None
Polysulfone	41	>73	76.6	16.5
Polyethersulfone	50	>73	92	9
Polyarylsulfone	41	>73	70	21
Polyphenylene sulfide	38	>73	84.5	28.5

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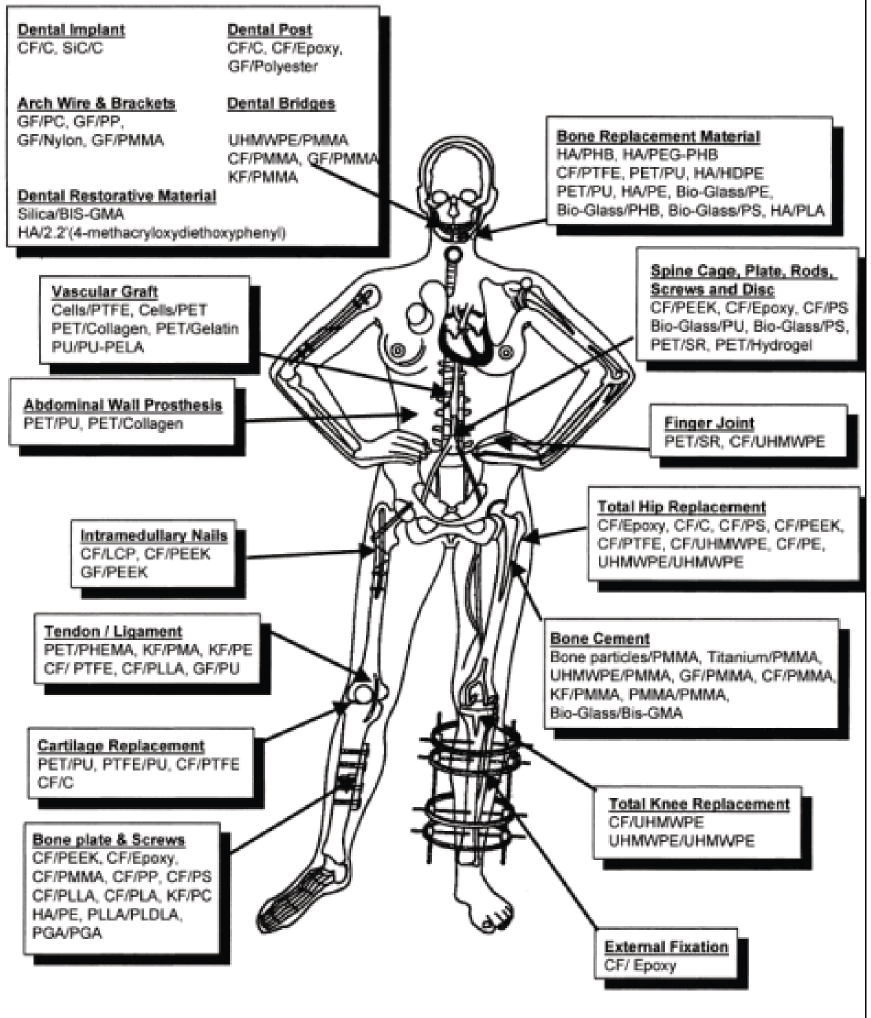

CF: carbon fibers, **C**: carbon, **GF**: glass fibers, **KF**: kevlar fibers, **PMMA**: Polymethylmethacrylate, **PS**: polysulfone, **PP**: Polypropylene, **UHMWPE**: ultra-high-molecular weight polyethylene, **PLDLA**: poly(L-DL-lactide), **PLLA**: poly (L-lactic acid), **PGA**: polglycolic acid, **PC**: polycarbonate, **PEEK**: polyetheretherketone; **HA**: hydroxyapatite, **PMA**: polymethylacrylate, **BIS-GMA**: bis-phenol A glycidyl methacrylate, **PU**: polyurethane, **PTFE**: polytetrafluoroethylene, **PET**: polyethyleneterephthalate, **PEA**: poltethylacrylate, **SR**: silicone rubber, **PELA**: Block co-polymer of lactic acid and polyethylene glycol, **LCP**: liquid crystalline polymer, **PHB**: polyhydroxybutyrate, **PEG**: polyethyleneglycol, **PHEMA**: poly(20hydroxyethyl methacrylate)

The various applications of different polymer composite biomaterials

Fig. 9.1. A representation of synthetic body parts already used as implants

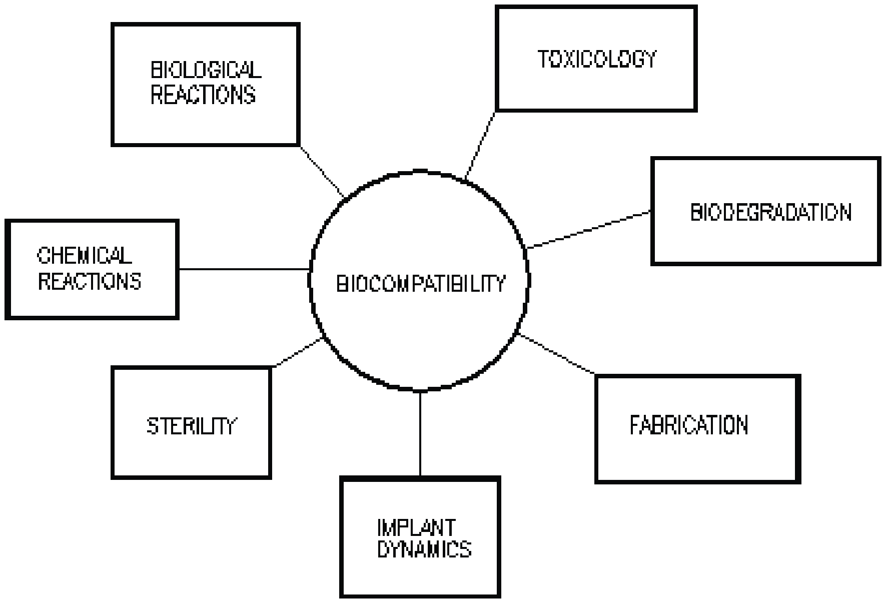

Fig. 9.2. Interaction of a biocompatible surface with the body

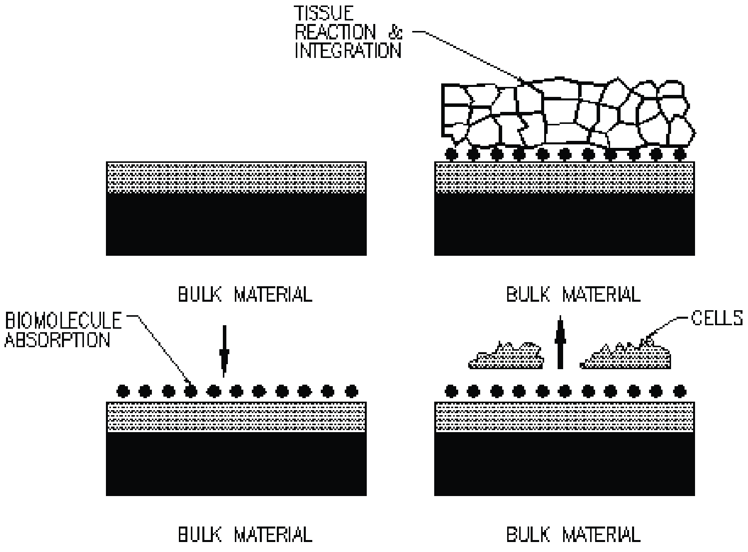

Fig. 9.3. Interaction between biomaterials and body tissues

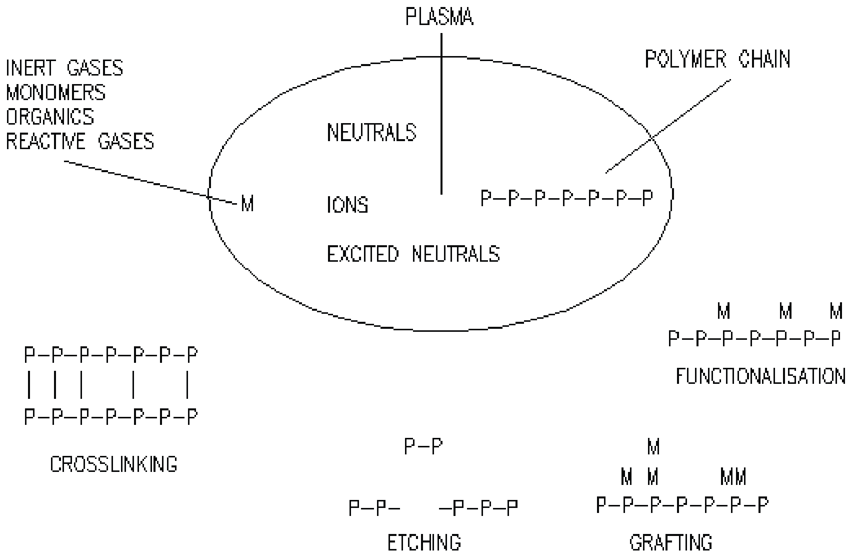

Fig. 9.4. Schematic diagram of the basic processes relevant in biomedical surface modification

Fig. 9.5a. Photograph of the Sterrad system (Photo courtesy Advanced Sterilization products, USA)

10. Emperor's New Clothes

Plasma treatment of Textiles

Textile Manufacturing was one of the early industries, which formed part of the industrial revolution. Since then, significant new developments are taking place in textile industry to meet the changing consumer tastes and increasing environmental pressures. Plasma processing has had a rebirth in the textile arena, with the earlier unsuccessful approach of using vacuum plasmas replaced by novel atmospheric pressure plasma. The process has ability to modify woven and non-woven textile surfaces to improve their properties. This chapter will discuss the role of plasma processing in the textile industry

Changing Trends in the Textile Industry

The textile industry is a major source of employment and wealth generation with a strong multiplier effect on diverse industrial sectors such as engineering, polymers, chemicals and dyestuffs etc. The market drivers of textile technology in the 1990s and beyond include greater emphasis upon design and innovative fabrics and the industrialized countries are attempting to reverse the long-term decline of their textile and clothing industries by investing in new technologies. The newly industrialised countries in East Asia, initially responsible for penetrating the Western markets have started to find themselves being displaced by a newer generation of developing countries. Technology is the key in this competitive struggle by companies and nations to maintain their share of the total value created throughout the entire chain of textile industries. Most countries with significant clothing industries have their own R&D centres, which are engaged upon a wide variety of incremental and fundamental research activities.

USA and Japan still provide the best examples of concerted programmes involving industry, academic organisations and government guided by a vision of a radically different long-term future for the textile and clothing industries. The US textile and clothing industries consist of more than 26,000 companies representing 2 million jobs - nearly 12 per cent of the entire manufacturing work force. Annual sales are more than $200 billion and contribute $53 billion to the GDP. In 1993, The US Government set up the AMTEX Partnership, a $ 500 million, five year programme of collaboration between the US Department of Energy, selected universities and the industry. The overall vision is of creating a modern industry that will become a dominant global force in providing high value products to the world market in an environment of growth, environmental responsibility and profitability. The programme was designed to exploit 'spin-offs' from prior government investments in science and technology.

The textile industry in India is one of the oldest industries. It is the second largest in the world. It provides direct employment to nearly 30 million people. Yarn exports crossed 554,000 tonnes in 1999-2000 valued at Rs. 700 billion [Hindu 2002]. Technical textiles offer an excellent opportunity or new direction with an average growth of 4 per cent expected during the period 1995-2005. However, India’s effort at modernisation and indigenous research and development in acquiring modern technology is relatively minimal.

Plasma Effects on Textile Substrates

The textile industry has long recognized that, the surface properties are a key for a large number of processes and applications and often need to be quite different from those of the fabric bulk. Surface properties determine enhancing dye uptake and colour fastness; reducing textile finishing, printing and coating costs; improving the bonding and adhesion properties of coated and laminated fabrics and sterilisation and optimizing bio-compatibility essential for medical implants containing wet liquid chemical processes. The conventional techniques are intrinsically costly and environmentally unfriendly because of the large amounts of energy involved and the consumption and contamination of large quantities of water. In addition, these processes treat the fabric bulk, which may adversely affect overall product performance. The industry is, therefore, strongly motivated to seek alternative surface engineering processes, which could offer lower cost, environment-friendly manufacturing routes to new products, with improved lifetime, quality and performance.

The chemical functionality and/or the morphology of a fibre surface can be altered in order to improve very different properties to tailor them for certain demands. Ablation of the fibre surface results in introduction of texture due to development of small cracks and fissures. The wettability can be increased to achieve a better impregnation or a deeper dying or, in contrast; it also can be decreased to create a water-repellent behavior. New chemical functionality on the surface can promote the reactivity with dyes. The adhesion in laminates can be largely enhanced. Water-free removal of sizing seems to be possible. These are only a few examples that demonstrate the potential of this technology.

The alterations of surface properties obtained by a plasma treatment are complex. Particle-induced reactions take usually place in the upper ten nanometers of a surface. Short wavelength UV-radiation as it is emitted by plasmas initiates reactions in a thicker layer of the order of 100 nm. The process gas and other process parameters can control the relation between the two and the extent of both. The outermost surface, only some atom layers, sometimes less than 1 nm determines the interaction with other media. The chemical composition of this part of a fibre is responsible for good or bad adhesion in laminates or determines whether the fabric is suitable for impregnation or not and this very part can be modified by plasma. For the success of the treatment it is not only the process parameters that are crucial, but also the original surface. Trace amounts of sizing, for example, can modify the reaction condition substantially and have to be taken into consideration for almost every process.

Plasma treatments have been used to induce both surface modifications and bulk property enhancements of textile materials, resulting in improvements to textile products ranging from conventional fabrics to advanced composites. These treatments have been shown to enhance dyeing rates of polymers, improve colourfastness and wash resistance of fabrics, and change the surface energy of fibres and fabrics. Research has shown that improvements in toughness, tenacity, and shrink resistance can be achieved by subjecting various thermoplastic fibres to a plasma atmosphere. Recently, plasma treatments have been investigated for producing hydroscopicity in fibres, altered degradation rates of biomedical materials (such as sutures), and for the deposition of antiwear coatings. The categories of plasma applications for textiles are shown in Fig. 10.1.

The plasma treatment of polymeric material has many advantages compared with classical wet chemical finishing. The main advantages are:

- Optimization of surface properties of materials without alteration of bulk characteristics.
- On polymers, which are unable or very difficult to modify with wet chemicals, the surface properties can also easily be changed.
- The consumption of chemicals is very low due to the physical process
- The process is performed in a dry, closed system, and excels in high reliability and safety
- Is environmentally friendly

Other advantages of plasma technologies stem from the underlying physical process. The traditional liquid chemical processes used by the textile industry involve high consumption - and pollution - of water resources. Waste-processing costs are also high and drying the processed fibres uses a lot of energy. This makes "dry" processing using plasma technology all the more attractive - especially from the environmental viewpoint.

Early Phase of Plasma Processing of Textiles

Since its introduction in the 1960s, the main industrial applications of low-pressure, cold plasmas have been in micro-electronic etching. In the 1980s, the applications extended to include surface modification of metals and polymers. A number of research laboratories in the textile industries and academic institutions began experimenting with vacuum plasma processing for a range of applications based on the understanding it had gained from surface treatment of polymers.

In 1974, Lee and Pavlath [Lee 1974] found that oxygen plasma was quite effective in shrink proofing wool fabrics knitted from plasma treated yarns. Shrinkage control increased nonlinearly with increasing power until saturation. Moreover, wettability changes have been extensively studied using CF_4 plasmas [Yasuda 1984]. Research results demonstrate that wettability is dramatically decreased leading to the possibility of imparting water repellant characteristics to fabrics. Traditionally wettable fabrics such as cotton or silk can be rendered completely water repellant. This can be done by implanting fluorine atoms as indicated by ESCA measurements of the treated surfaces.

New Initiatives in Plasma Textile Technology

Low pressure plasma technology never got a foothold in textile processing because of a fundamental incompatibility. Surface treatment with plasma is only one of the production steps and to ensure overall throughput the speed of this process step has to synchronize with the other processes, which happen at 20 m/min. Moreover, sample size is limited by system configurations. The expensive, closed-perimeter vacuum system cannot be used for production lines, with machines processing fabric 2 metres wide at typically 2 m/min. speed. Although some air-to-air and cassette-to-cassette batch-continuous processing systems have been developed, there are still no cheap and effective on-line systems. Prominent manufacturers of such equipment include Metroline Industries, Airco coatings Inc. and Technoplasma SA [Shishoo 1996].

Atmospheric processes are essential for industries requiring large throughput such as the textile industry. The Plasmatex project in Europe was aimed at developing a complete atmospheric pressure plasma processing system, which would allow the potential for plasma treatment of textiles and non-wovens to be realised on an industrial scale. The scope of the project would include the plasma equipment itself; the necessary fabric feed and take-up equipment; and supporting background plasma characterisation and modelling data. In particular, the detailed objectives were to develop an atmospheric pressure plasma system (APPS), which could be evaluated and shown to be effective in at least one of a range of process and product improvements.

The most common atmospheric pressure plasma systems used in textile industry are derivatives of the generic barrier and corona discharges. However, these discharges produce useful plasma conditions only in small volumes permeated by the streamers resulting in limited areas of the fabric surface getting treated. Corona plasmas also cannot penetrate deep into yarn or woven fabrics. The outcome of this is the low processing speed, typically 1 meter/min. The atmospheric pressure glow discharge systems have effectively higher speeds of processing, larger by a factor of 100.

The Plasmatex project, which started in February 1997 and closed at the end of April 2000, involved a broadly based team with membership representing research, equipment manufactures and textile-processing interests. The detailed industrial objective of Plasmatex is to develop new plasma systems, which can carry out one or more of the following processes with a high degree of manufacturability demonstrated by continuous, on-line treatment of endless lengths of fabric on spools.

1. Antifelting of wool
2. Enhance dye uptake and fastness
3. Reduce costs in textile finishing, printing and coating
4. Improve dyeing of yarns and warp/weft knitted fabrics
5. Improve the functional properties of nonwovens
6. Improve the properties of forming and dryer fabrics/press felts for paper manufacture
7. Improve the bonding properties of coated and laminated polypropylene

The Swedish Institute of Fibre and Polymer Research (IFP) and Queens University of Belfast participated in fundamental studies on surface modifications and the modeling and characterisation of plasmas. Plasma Ireland was responsible for the development and construction of three prototype atmospheric plasma systems. For industrial scale evaluation, these prototypes were made available to six companies, covering a diverse range of textile products and processing interests. Almedahls Borgstena Textile and SCA Hygiene Products evaluated the effect of the process on cotton and cotton-polyester woven fabrics, car upholstery polyester fabrics and wet-laid non-wovens. Kirchoff in Germany used the second unit to assess whether plasma treatment would eliminate problem of felting in woolen fabrics. Spanish company Polisilk determined whether adhesion characteristics of polypropylene fabrics could be improved. The Scapa Group in the UK used the third unit for testing the effects of plasma treatment on various specialized fabrics, used as paper-machine clothing.

The project has been very successful, demonstrating the feasibility of atmospheric pressure plasma technology to work on an industrial scale and be effective in the surface treatment of textiles. The experience gained with the three prototypes has already been applied to the construction of a new unit and the group at Queen's University has come up with simple, reliable techniques to characterize the plasma during processing. Although the project reached a formal completion, there is an impetus from the team members for development work to continue. This would allow the range of materials treated to be extended and the process to be optimized - for example, in terms of line speed and gas utilization.

Plasmatex was set up to realize the potential of plasma technology as a means for treating fabrics industrially to achieve various surface functions. This technology offers a versatile approach with the potential to overcome the cost and environmental problems associated with current techniques for modifying fabric surfaces. The plasma modification of polymeric materials used as textiles, membranes, foils, non-wovens, composites, and so on and has been able to optimize a lot of commercially relevant properties.

Nonaqeous Techniques for Desizing

Water is one of the most important inputs in textile industry, during both conditioning of textile substrates and as a relational fluid during finishing. The average consumption of water per kilogram of textile processed is 100 litres [Rastogi 2003]. A typical mill consumes close to 2 million litres of water per day. With 280 composite mills and 2000 processing houses in India, the quantity of water consumed is gigantic [Jhala 1982]. The textile industry is coming under significant pressure to reduce or eliminate water consumption in all areas of fibre preparation, dyeing and finishing. In recent years, effluent treatment has become a major cost contributor driven by environmental legislation and the consumer. Legislation to tighten aqueous-based emissions is likely to increase. Hence, there is a need to develop environmentally safe, effluent-free processes with reduced processing costs.

Plasma, consisting of energetic particles generated by an electric field, can be used to strip the sizing material from the fibre surfaces, creating a highly energetic substrate surface. The focus of studies of non-aqueous fibre preparation and finishing involved the removal of starch from the surface of both glass fibres and fibreglass woven fabrics using various plasma techniques. This work was first conducted in a vacuum, and was transferred later to an atmospheric plasma device. After successful removal using both processes, finishing techniques were investigated using the vacuum apparatus previously mentioned. Thin film, diamond-like carbon coatings were deposited onto the samples leaving behind a lubricious, yet wear resistant surface.

Plasma Activated Dyeing and Finishing

The objective of the process is the realisation of a gaseous dye, which is capable of diffusion into the fibrous substrate without the use of water or surfactants. The novel dyeing process being proposed not only involves heat, but also involves the physical bombardment of energetic particles. This process will begin by grinding a pure, dry dye into a fine powder. The dye powder will then be applied to the substrate using a technique in which electrostatic charges will cause the dye particles to be attracted to the surface of the fibre. After coating the fibre with the dye particles, it will then be subjected to a high energy field. Bombardment of the dye particles with ions, electrons, infrared and ultraviolet radiation will vaporise the dye in a manner similar to that occurring in the thermosol process. However, this process is novel in the fact that the energetic species such as electrons and ions have the ability to alter the structure of the dye molecule. One can speculate that any dye chromophore that survives this intense high energy field would have superior sublimation, colour, and wash fastness over one that has been activated by thermal energy alone. Results from preliminary experiments have been favourable. The colour value of the dispersed dye survived the high-energy field and the dye penetrated the fibre.

Endless Fibre Surface Engineering

The market of conducting (metals) and insulating (polymers and ceramics) endless fibres is in the order of billions of tons. The majority of these endless fibres are surface treated to impart surface properties different to that of the bulk. This is normally carried out by environmentally detrimental wet chemical process.

The current revival of surface modification by plasma has come about as a result of improved scientific understanding of the chemical/electronic reactions involved as well as the development of necessary manufacturing equipment. Applying this new knowledge to endless fibre production will allow for industrially viable environmentally friendly plasma processes to be realised. Although the laboratory feasibility and flexibility of plasma technology is proven, there is no viable commercial equipment for the continuous clean surface engineering of high volume endless fibres yet available.

The objectives of the work are to realise the potential of plasma-based processing for endless fibre surface engineering by developing and demonstrating with prototype equipment and processes. This would offer a new industrially viable and environmentally friendly endless fibre manufacturing process. The subsequent enabling strategy will allow versatile surface engineering and the development of innovative products. The process would be applied to an actual fibre composite manufacturing facility and show its reliability in an industrial environment. Finally the plasma-surface engineered endless fibres in high volumes would be tested in the composite, biomedical and textile industries. This will demonstrate the advantages of this technology over the existing environmentally hazardous approaches.

Applications to Technical Textiles

Scratch resistant, transparent, uncolored coatings are needed both for polymers and chromium nickel deposited films, for applications in medical textiles. Transparent thin SiO_2 films can be deposited by PECVD from the precursors $SiCl_4$ or SiH_4 and using Oxygen as the carrier gas at high substrate temperatures. This precludes temperature sensitive substrates (like polymers, for example) from the treatment.

When siloxanes like hexamethyldisiloxane (HMDSO) and Oxygen are used as starting materials, quartz like films can also be generated at low substrate temperatures (about 50 °C). During film growth hydrocarbon molecule fragments (CH_2 and CH_3) are partly incorporated. Because of this, they are also called SiOxCy: H films. These films have to be adapted to different substrates in order to guarantee good adhesion and homogeneity of the films on three-dimensional formed parts. Therefore, the deposition in small grooves and the step coverage is very important.

Atomic Oxygen formed in the plasma (beside high energetic electrons) causes fragmentation of the HMDSO monomer and formation of volatile CO_2 and H_2O of the dissociated C and H atoms. The more Oxygen is used, the more quartz-like the films become.

Above a O_2/HMDSO ratio of 6 scratch resistant, transparent $SiO_{1.8}C_{0.3}$ films are deposited with excellent adhesion to polymer substrates like PC and PBT. The analysis of the chemical composition by XPS also reveals, that the films are grown in conformity to a SiO_2 matrix with a few Si and SiH:O bindings substituted by Si and SiH:CH2 or Si and SiH:CH3. A Taber test at 500 g load, employed by the industry to prove scratch resistance, exhibited a scattered light fraction < one percent. Moreover, the films have high densities (1.9-2.0 g/cm3) almost reaching the density of fused silica (2.2 g/cm3).

The plasma siloxane films on chromium nickel vapor deposits have to withstand contact with acetone and hydrous surfactant solutions, as well as scratching with a brass brush. Scratch resistant coatings on three-dimensional structures (deposition in small grooves and on tips) for medicinal technical applications are possible. Crucial for wear reduction is a total coverage of the structure by the SiOx film to avoid starting points for wearing of the rather brittle films.

Textiles with electromagnetic conducting properties are in demand for electromagnetic interference shielding for personal computers and home electronic appliances, flooring and ceiling materials, and in stealth technology [Heisy 1993]. Within the class of conducting polymers, polyaniline (Pan) has many electrical and optical properties with good stability [Wei 1989]. Plasma surface treatment is an effective method to increase aniline deposition on nylon 6 fabric. Oxygen plasma treated surfaces retained the highest conductivity and Pan deposit. The etching produces various functional groups such as COOH and C=O. The polar groups such as –OH and –OOH introduced during the process increased the conductivity [Oh 2001].

Treatment of Non-wovens

Polypropylene (PP) and polyester (PES) nonwoven fabrics are used in filtration media, battery separators, geotextiles, oil absorbents, baby diapers, disposable hygiene products, biomedical textiles etc. The most common way to produce nonwovens is spun bonding with typical production line speed of 550 meter/min. These materials are generally hydrophobic, whereas most applications demand water wettability. Traditionally, the hydrophilicity is imparted to these fabrics by spray coating them with aqueous solutions of surfactants.

Permanent hydrophilicity can be imparted to these fabric surfaces by Nitrogen plasma activation followed by post-plasma grafting using wetting in aqueous solutions such as acrylic acid and grafting completed at 60^{o}C. Cross-linking produced by the plasma is considered to inhibit the hydrophobic recovery. This does away with organic solvents and the associated environmental problems.

Spun fabrics pose special problems for plasma processing. For the plasma to penetrate the pores, the Debye length has to be smaller than the average pore size, which is of the order of 10-100 µm. This condition can be fulfilled in atmospheric pressure plasmas. Nonwovens have been effectively treated by surface discharge plasma sources, where high density streamers are produced across an insulator surface between metallic electrodes [Simor 2002]. In this way the streamer gets into better contact with the fabric surface and improves the effectiveness and speed of processing. Electrical energy requirement is quantified at 0.3 kWh/kg with processing speed of 100 meter/min [Gulejova 2002].

Metal-Coated Organic Polymers

Metal-coated organic polymers are used for a variety of applications in many types of industries. If the metallized polymer is to fulfill its function, it is essential that the metal adhere strongly to the polymer substrate. This can be obtained by a plasma pre-treatment of the polymer. For example: Oxygen plasma treatment of ABS before copper deposition by evaporation

Good adhesion between fibers and matrix (or laminates) depends upon the surface characteristics of fibres, matrix and the physico-chemical interactions taking place at the interface. A prerequisite condition of good adhesion between fibre and matrix remains the surface energy of fibers, which must be higher or equal to the surface energy of the matrix. This can be achieved with plasma treatments.

Plasma Treatment with Liquid Precursors

By combining atmospheric pressure plasma systems developed by Plasma Ireland Ltd with a unique precursor delivery system, Dow Corning has developed a new coating process using liquid precursors [Herbert 2001]. Parallel plate reactors driven by 10 kV peak-to-peak 30-50 kHz pulses at 1 W/cm^2 produces a plasma in a helium environment into which monomer liquid is introduced. The precursors may be chosen from a range of polymer precursors, organic materials such as acrylates and alkenes. Tetramethylcyclotetrasiloxane and octamethylcyclotetrasiloxane have been used to produce polysiloxane coatings, which have excellent hydrophobcity. Using the same monomers, but changing to an oxidizing condition, hydrophilic coatings have been obtained. Perfluorocarbon monomers have been polymerized to produce oil resistant coatings.

The prepared materials are then be subjected to a novel, non-aqueous, surface finishing technique, which will be used to deposit lubricious, low coefficient of friction coatings. This coating has been shown to reduce the leaching of oligomer and small molecules from polymeric material. The aim is to eliminate the need for treatment with silicone or other low friction coatings currently being employed to combat sewing needle heating and breaking in apparel manufacturing.

A state-of-the-art nonaqueous methodology is provided that has potential to provide for novel fibre preparation, for example, descouring and desizing, fibre coloration using low and medium molecular weight dyes, and finishing. In the case of fibre finishing, fibres can be coated for enhanced wash fastness and crock fastness, improved handle and strength. In particular, reduction of frictional properties can lead to reduction of hairiness and fibrillation, thereby improving appearance. Furthermore, it is anticipated that by design of the coating material to absorb ultraviolet light, enhanced light fastness of both the fibre and dye would be achieved.

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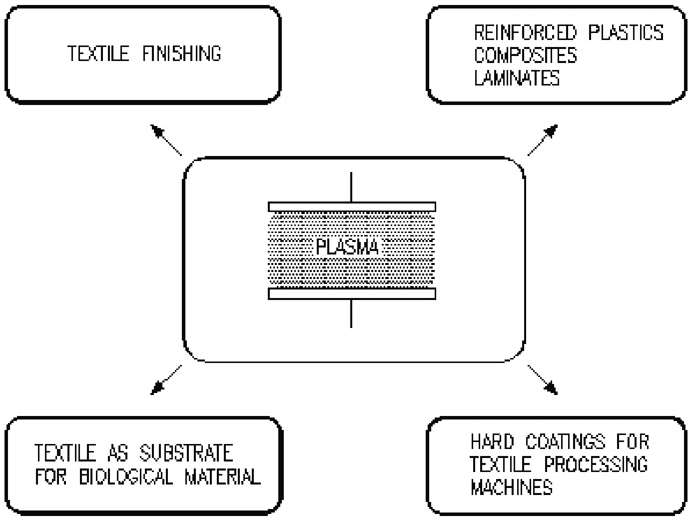

Fig. 10.1. Role of plasma processing in textile technology

11. The Glassified PET

Barrier Coating on Food Packaging

Techniques of packaging food have evolved over centuries. The prevailing method at the present time is to use synthetic organic films for food packaging. The films are generally prone to permeation of air spoiling the packed food. Modern plasma assisted thin film coating technologies play a major role in manufacturing barrier films for food packaging. This chapter discusses some of the techniques.

Food Packaging

In the southern Indian state of Kerala, food articles are traditionally packed in banana leaves, made pliant by steaming. Banana leaf can be called an active packaging since it infuses the packed food with its own aroma, and a nice one too. But today, food packaging has travelled from banana leaves to PET (Polyethylene terephthalate), going full cycle from natural to synthetic organics, driven by consumer preferences, the changing nature of both food and life-styles. In between there were trysts with earthen pot, glass and metal. Glass blowing invented by the Phoenicians in 3rd century BC created crude glass bottles. Sealed and sterilised tin containers preserved food for long periods. Aluminium foil containers appeared in 1950s while the aluminium can appeared in 1959. Food products started using collapsible, soft metal tubes in the 1960s. The Polyethylene Terephthalate (PET) container only became available during the last two decades. Its use for beverages started in 1977. By 1980, foods and other hot-fill products such as jams could also be packaged in PET.

Food packaging has many functions. It provides visual appeal to the packaged food and identifies the manufacturer. Most important role of packaging materials is to provide protection to packaged foods against harmful environmental factors. However, the functional consideration arising out of the fact that food is essentially perishable by nature is to contain and preserve the packaged product and extend its shelf life. Food deteriorates by physical, biochemical and microbiological routes independently or in concert [Man 1997]. The perishability derives from chemical changes, which include oxidative reactions, lipid oxidation, and enzymatic actions as well as microbiological attack. All of these can degrade food and make it unfit or unsafe for human consumption. The interaction between packaged food and the environment is depicted schematically in Fig. 11.1.

Packaging material must fulfill many specifications. If the physical or chemical deterioration is related to the equilibrium moisture content, the barrier properties of the package relating to water vapour will be of major importance in maintaining or extending shelf life. The Oxygen concentration in a permeable package will directly affect the rate of oxidation of Oxygen-sensitive nutrients such as vitamins, fatty acids and proteins. The loss of specific aroma or flavour constituents due to permeation can also lead to a reduction of product quality. Microbiological action accelerates in the presence of Oxygen content in the package or with the permeation of fresh Oxygen into the package. The acceptable levels of Oxygen permeation is given in Table 11.1. Packaging is also sensitive to modern eco-environmental concerns. The minimization of material to meet the basic function as well as being amenable to collection and recycling are major aspects of this concern.

The Problems with Polymers

The modern packaging materials are made from polymers such as polyethylene (PE), polypropylene (PP) and polyester (PET) and made into thin films and foils.

These materials are relatively permeable to small molecules making up gases, water vapour, organic vapours, and liquids. In packaging with polymer structures, these gases and vapours from flavour and aroma compounds, additives, and low molecular weight residual moieties etc may transfer from either the internal or external environment through the polymer package wall, resulting in a continuous change.

Gas permeation through these materials is through diffusion of gas molecules, a process of random movement with an overall direction driven by the concentration gradient [Hennesy 1966]. Many factors determine the nature of diffusion of gases through solids. The crystalline structure of the material, the degree of crystallinity, presence of pinholes and other defects, polarity of the gas and solid as well as possible chemical reactions between the solid and the gas control the barrier properties. There is a correlation between free volume hole size and permeation [Stocksiefen 1995] with polyesters and copolyesters having low permeability, in addition to being chemically stable and biocompatible. Permeability is a property, which is material-dependent and is a measure for the ability of specific gases to permeate or diffuse through this material. Permeability in the packaging context is defined as the product of thickness and transmission Rate (cc-mil/m^2 day atm at R.H. at 0^o C) (mil) x (cc/m^2 day atm at R.H. at 0^o C). Our understanding of this process is essentially empirical.

The varying resistance of polymeric thin films to the permeation of gases is compiled in Table 11.2.

Polyethylene terephthalate, commonly known as PET made its commercial debut in 1974. It has now become the preferred packaging material and is a ubiquitous part of the 21st century supermarket landscape. PET has replaced glass as the standard packaging for products such as carbonated soft drinks, bottled water and cooking oil. PET has many advantages in terms of strength, clarity, lightness and low cost. However, it has a major limitation due to its permeability to Oxygen and CO_2, which makes the PET container unsuitable for sensitive products like wine and beer, which demands extended shelf life. The problem is further compounded by the fact that gas permeability is directly proportional to surface area. Hence smaller the container, the greater the rate of gaseous passage and product degradation.

Industry is experimenting with various ideas to enhance the gas barrier properties of PET and other relatively inexpensive polymer packaging materials. By increasing the degree of crystallinity through orientation or heat treatment, it is possible to significantly reduce gas permeability. CO_2 and O_2 barriers can be built into PET bottles using a multi-layer structure sandwiching PET structural layers around a core layer or layers containing higher-priced barrier materials. Promising new barrier materials are Nylon-based nanocomposites and active Oxygen scavenger barrier systems. The cost of building up such a multilayered polymer sandwich is high, especially since the new barrier materials are expensive. The high price of PEN and PEN/PET blends currently prevents widespread adoption for single-use containers. Polyvinylidene chloride (PVDC), commonly known as Saran and ethylene vinyl alcohol (EVOH) are generally key components of high-barrier films.

Technology Drivers for Barrier Coatings

Polymer properties can be improved by addition of an inorganic film on their surface. The inorganic film can serve as a gas diffusion barrier, as well as strengthen the polymer. But this barrier material must also fulfill the requirement that it should be easily removable during recycling. To gain high value added markets, the recycled PET must be almost entirely free of contamination. Another issue is the machinability of such hard films. The elasticity of SiOx layers have been significantly improved by combining a PVD process with plasma polymerization, depositing organically modified SiOx-coatings. The resistance to micro cracking behavior has been improved from 0.8 per cent for pure PVD coating up to 2 per cent for organically modified SiO_x layers. Due to the high deposition rates of some 100 nm/s, coating cost of 3 to 7 $/m² can be achieved.

The functional properties that should be fulfilled by thin film coatings to be useful in food packaging applications are:

- High transparency
- Water vapour transmission rate of 1 gm/m² day or better for a 12 micron coating
- Oxygen transmission rate of 5 cm³/m² day bar or better for 12 micron coating
- The coating must retain its barrier properties during process of conversion into the final product
- The compressive stress of the film should not exceed $5x10^9/cm^2$ to avoid cracking
- The coating should provide abrasion resistance to the soft plastic film during pre and post coating handling
- High coating rate

Transparent barrier films became first known with a Dupont patent in 1969 [Weinert 1994]. In the absence of roll coaters at that time, the invention remained a laboratory curiosity. Several types of coatings, which meet the above requirements, have been developed for food packaging. These include 1 - 6 µm thick SiO_x and Al_2O_3 as well as carbon film coatings. The development of the coating process has taken two directions. In one, the traditional thin film web-metalizing process has been modified into handling oxide coatings. In the other, the finished products like bottles or containers are coated either inside or outside.

Among the applications of thin film coating, the coating of packaging products dominate as shown in the market share for different applications given in Fig. 11.2. The enormously large volumes to be coated to satisfy the large processed food market and the cost of coating are the prime technology drivers. It is estimated that 15 billion square meter of polymer films are coated per year worldwide [Langowski 2001], out of which food packaging accounts for two thirds of the overall volume. The annual growth has been 8-12 per cent over the last decade. The high barrier packaging market in the United States has been experiencing sustained growth of nearly 10 per cent on an annual basis for the last several years, and future growth is expected to be strong. In addition, a new market perspective is seen in transparent barrier layers on the basis of oxides from Silicon and Aluminium, made at present mainly in Japan.

Consequently, a number of industry-research consortia have emerged to meet the demands for a commercially viable process and technology. In the CRAFT project, a group of 10 industries collaborated under the leadership of Fraunhoffer Institute for Process Engineering. The research integrates the proprietary coating processes of the partners into the production chain of high barrier coatings as film production. The main objective of this project was to co-ordinate the industrial R&D activities ongoing in different companies and to achieve a better collaboration between industrial partners specialising in the following production steps:

- Pre-treatment of substrate films (corona, flame, plasma)
- Vacuum coating (Al, SiO_x and AlO_x)
- Final lamination (adhesive and extrusion)

Simple barrier films, consisting of metal or ceramic oxide layers vapour deposited on polyester or polypropylene, have been developed and successfully utilized in flexible food packaging applications. However, substrate roughness and defects intrinsic to these materials limit their barrier performance. Vapour permeation rates fall as a function of deposited barrier film thickness due to the covering of substrate roughness and the filling of pinholes. The propagation of grain boundary defects results in no significant gain beyond a critical thickness, which is typically 100 - 300 Å, resulting in a lower limit of transmission rate of ~ 0.05 g/m^2 /day. [Fayet 1995] Furthermore, most vapour deposition techniques are conformal, reproducing the substrate texture. Breaks in continuity as the film traverses high aspect ratio features on rough substrates can also limit the effectiveness of vapour-deposited coatings on plastic.

$SiO_{1.8}$ is the widely used glass barrier coating because of its unusual glass-forming ability. The film is polymer-like and the lower Oxygen stoichiometry improves barrier properties. It has flexible bonds, which imparts high elongation for the coating and resistance to crystallisation during coating. The low refractive index inhibits glare from the surface. The Oxygen transmission of coated film is in the range of 0.02-0.06 g/100 square inch/day and the water vapour transmission is 0.05-0.07 g/100 square inch/day. Additives like oxides of Magnesium, Barium, Boron, Germanium, Zinc and Titanium can enhance the barrier and chemical resistance properties. For example, glass containing 35 per cent Magnesium has lower melting point, which allows the film to anneal and increase its packing density before it solidifies. 10 per cent Zirconium can make it resistive to alkali and acid attack.

The barrier coating can be applied externally or internally. The choice is determined by a number of considerations. Different areas of a PET container have different gas permeability, due to variances in the extent of biaxial orientation of molecules within the plastic itself. External coatings are more prone to mechanical damage. However, they give an option of introducing a second process to increase the coating's resistance to scratching. Internal coating has the added advantage of providing a barrier to migration from the bottle material itself. However, the coating being in contact with the product, their mutual interaction must be considered. Internal coatings on refill bottles are subjected to very aggressive cleaning processes, which may cause the coating to break away. Vacuum based internal coating systems also require the outer chamber to be evacuated in order to prevent the bottle from collapsing

Polymer surfaces must be treated to ensure adhesive bonding and to promote good mechanical and optical properties. An important factor that determines the quality of the vacuum deposited barrier layer is the condition of the substrate surface prior to coating. Many of the commonly used polymers exhibit a low degree of surface energy, inhibiting the creation of a good layer of barrier material during the coating process. Interaction with energetic ions, free radicals, electrons, and neutral particles can modify surfaces to a depth of a few molecules. The surface modification can not only remove adherent contaminates such as organic materials; it can also produce functional polar groups which promote covalent bonding, and densification through cross-linking. A corona discharge is often used in web coating and is effective and economical for many polymers. Newer processes of surface treatment involve ionisation of various gas mixtures in a RF field depending on the application and DC magnetron sputtering. Surface oxidation, nitration, amination or hydrolyzation can be produced to enhance surface energy to promote bonding. The surface morphology of the chosen substrate also plays a role in the properties of the barrier layer; a smooth, flat substrate gives better barrier.

Web Coating Processes

Many thin film coating processes developed primarily for more demanding applications in optical devices and surface engineering products have been adapted to barrier coating applications. These are primarily reactive sputter deposition or electron beam evaporation of Aluminium or SiO_2 [Hoffman 1994, Lohwasser 1995], Plasma Enhanced Chemical Vapour Deposition (PECVD) of SiO_2 [Fayet 1995] and diamond like Carbon coating by PECVD reactive evaporation. A schematic diagram of the PVD process in the web-coating context is given in fig. 11.3.

To achieve significant barrier improvement with thin film metal or oxide coating, surface pre-treatment with active Oxygen is usually employed. Oxygen plasma generates active surface groups, which allows good nucleation and adhesion properties for the build up of the films. In addition, the Oxygen plasma improves the topography of the surface and decreases defects.

Pulsed Magnetron Sputtering is one of the most exciting developments in the field of sputtering in the 90's. Plasma-activation during evaporation significantly improves layer properties at high deposition rates. In the Dual Magnetron Sputtering, two magnetron sources are connected to a bipolar pulse generator so that each magnetron alternatively acts as the cathode and an anode of magnetron discharges [Metzner 1996]. This process significantly reduces arcs prevalent in dielectric coating with the result that reactive sputtering of oxides at high rates becomes possible. The reactive sputtering of oxides lead to the formation of negative ions of Oxygen, which, accelerated by the cathode fall, impinge the substrate with high energy. As a result, very dense layers with high hardness are deposited [Schiller 1999]. The improvement in the barrier properties is linked to the energy of the condensing particles. Considerable work on further development of this technology to suit industrial application is progressing in many laboratories [Schiller1994, 1995, Fenn Jr. 1998].

Evaporative PVD is done in an atmosphere permeated by metal vapours produced by arc evaporation on a metal surface or by irradiating the surface by electrons beams produced by hollow cathode discharge [Fig. 11.4]. The very high density that can be produced by electron beam discharges is due to the magnetic trapping of the primary electrons by a longitudinal magnetic field [Schiller 1982]. Low energy electrons produced by the ionisation of neutral atoms and scattering of the energetic electrons along with the ions diffuse across the magnetic field and permeate to the substrate region. The layer microstructure is influenced by the mean kinetic energy of the condensing particles, and improves with the degree of plasma activation. The layers have low intrinsic stress because the depositing particle has low energy, of the order of 15-20 eV. Deposition rates of 100 nm/sec are common

Hollow Cathode Activated Deposition (HAD) process is based on the reactive evaporation of oxide or metal at high rates in combination with a hollow cathode plasma activation. The hollow cathode plasma source generates an arc discharge plasma with very high plasma densities of the order of 10^{12} cm^{-3}. For insulating substrates, a high self bias potential of about 15 V is obtained. The typical deposition rates are 100 - 150 nm/s for Al_2O_3 and 300 – 600 nm/s for SiO_x. The deposited layers show a dense, amorphous structure. The microhardness is typically 6 GPa for Al_2O_3 layers and 3 GPa for SiO_x respectively. Both oxides perform well against abrasion.

Bottle Coating Processes

Silicon vapour can be oxidised in oxygen plasma to SiOx. The anodic arc process uses expendable Silicon metal contained in a crucible as the anode of a vacuum arc [Ehrich 1990]. DC voltage of 20-30 V is applied between a metal cathode and this crucible, resulting in a continuous arc discharge between the cathode and the anode as long as there is a vapour cloud in front of the cathode. This discharge generates highly activated plasma inside the vacuum chamber, where Si atoms with a high excitation are evaporated towards the substrate rotating above the vapour cloud. Oxygen is added to the vapour, resulting in a deposition of SiOx on the surface of the substrate [Fig. 11.5].

The process has been commercialised by Applied Films together with Krones AG, Germany and Coca Cola Company, US [Budke 2001]. In the production line coater, there are six vacuum arc evaporators and a novel load lock arrangement to introduce large number of bottles into the vacuum system for coating. The bottles traverse the evaporators twice at a speed of 0.47 m/second. The coating time to deposit the glass-like layer is 1.27 sec per bottle. With 20,000 half-litre coca cola bottles coated per hour, this system is perhaps the fastest bottle coating system at present.

Plasma polymerisation is the process of building up polymer-like layers of organic or inorganic materials on substrates [Biederman 1992]. This process belongs to the class of plasma enhanced chemical vapour deposition processes (PECVD). In PECVD, the vapours of the desired ingredient are introduced into a plasma where the electrons ionise or fragment the molecules into radicals [Fig. 11.6]. These active molecules can undergo chemical reactions on the surface or in the vapour phase and finally deposit as films. The nucleation process depends on the surface morphology and presence of foreign atoms on the surface. These dense films are hydrophobic and pinhole free. But the process parameters have to be optimised to obtain good quality films in short time, required typically in barrier coating applications [Knoll 1995]. Plasma deposited organo-silicon films can be deposited by dissociating Silicone resins in a plasma and reacting the Silicon atoms with Oxygen, Nitrogen or their combination to deposit silicon dioxide, silicon nitride or silicon oxynitride films. The precursors for diamond like Carbon films are organic gases like acetylene.

Plasma Impulse CVD (PICVD) process is a significant improvement over conventional CVD. The plasma is pulsed by pulsing the power source, typically RF or microwave, which then, allows for ions to reach lower energies during the coating process. The coating is built up in a series of small steps, which produces an extremely dense and homogeneous coating. Moreover, the chemical composition of the reaction mixture can be changed between pulses. Consequently, during the course of one process operation, different layers can be combined to produce a made-to-measure multilayer system. PICVD process for SiO_2 and TiO_2 has been applied to a broad range of plastics (e.g. PET, PMMA, PC, COC, PP and HDPE).

Diamond like Carbon coating has also been used in barrier films. The coating process consists of the deposition of a very thin, diamond-like layer of carbon on the interior of the PET container. The bottle is first enclosed in a vacuum chamber. Acetylene (C_2H_2) gas is then injected into the bottle. Radio frequency energy is next applied to create a low temperature plasma state. The Carbon ions coalesce on the inner surface of the bottle in an amorphous structure. Finally, waste gases are purged with nitrogen before the newly coated bottle emerges from the chamber. The final thickness of the coating is between 0.02 and 0.04 microns. The prototype machine runs on an 18-second cycle, producing 1,600 bph from eight cavities. Plans are already underway for a second machine based on the HBB-8, but with an output of up to 2,400 bph.

The coatings produced by plasma polymerisation of acetylene exhibit a yellow brown coloration, which during trials was of assistance in optically assessing the thickness and distribution of the coating. Other substances, principally those containing Silicon, can be used equally successfully, under different process parameters, to produce a more transparent coating. However, the brownish colour is considered an advantage in certain applications where the contents of the bottle also require UV protection.

The basic process for applying an internal plasma polymerisation coating works in the following way. The bottle, inside a vacuum chamber, is held upside-down in a nest and is sealed at the neck. The chamber is closed, and the pressure reduced to a level of 1 – 10 Pa, at which point a suitable gas or gas blend is introduced into the bottle. The chamber is subjected to microwave radiation, which enters via the PTFE windows seen in Fig. 11.6. There is no plasma generation in the hard vacuum outside the bottle and the microwaves pass through to the inside of the bottle without loss. Inside the bottle the conditions are such that the monomer gas is excited to a plasma condition and becomes polymerised. The film is deposited in a micro-fine layer on the internal walls of the bottle. A number of manufacturers -Glaskin (Tetra Pak) and Actis (Sidel) – use this principle, though with different process gases to produce different coatings.

In the prototype, the vacuum chamber was made from a stainless steel T-shaped tube, with an observation window. It is possible to make the chamber from a suitably sized glass tube with a metal mesh to act as a microwave shield. The system described could be adapted to carry out both processes in sequence by diffusing gas into the inside of the bottle and adding a second microwave source in the vacuum chamber

Varying the gas composition and the pressure while maintaining the microwave energy level constant can also control the overall thickness of the coating. The moisture vapour transmission rate is also reduced. The appearance of the finished product is also highly favourable, with the bottle retaining a high gloss and transparency and a slight amber tint. For products such as beer, which are light sensitive, amber coloured PET bottles would have to be used, so the coating would not be apparent to the consumer. With barrier properties comparable to glass, products such as beer, wine and mayonnaise can be packed in smaller PET bottles.

To integrate the PICVD coating of plastics containers in an economic mass production system, the machines operate on a continuous flow basis. The containers are loaded into the vacuum chambers in rapid succession and the internal coating - a bonding agent layer plus the SiO_2 barrier layer - is applied. A complete coating cycle lasts no more than a few seconds. To guarantee the layer quality on a long-term basis, the whole process is subject to comprehensive monitoring - from the gas composition of the plasma via the process parameters right through to long-term stability including temperature, pressure and gas flow. This also includes monitoring maintenance and service routines.

Bottles are fed into a vacuum chamber through a system of airlocks, on a continuous basis. The disadvantage of this process is the significantly lower pressures that are required when compared with plasma polymerisation. There is also the problem, when applying external coatings, of the chamber and equipment itself becoming coated over time.

Expanding Markets for Barrier Films

Of late, barrier films are finding applications beyond food preservation. With reduced gas permeation, the films can act as corrosion resistant and anti-tarnish coatings. They can also improve the storage properties of gas containers. Some of the important applications are discussed below.

Highly polished metal surfaces are good broadband reflectors. The best metallic reflectors are made by deposition of thin coating of metal on a polished substrate. Metal mirrors have been made for centuries and are fairly common in many optical systems. The mirror's main purpose is to collect light and steer it to another location in the optical system. Metal mirrors offer high efficiencies and are the coating of choice for very large optics, such as telescope mirrors. Unfortunately, the freshly deposited metals tarnish very quickly with the formation of oxides or other compounds, as a result the reflectance drops dramatically.

To prevent significant loss of reflectance, metal films require an overcoat with thin dielectric films. The most common metals used for highly reflective surfaces are Aluminium (Al), Gold (Au), and Silver (Ag). There are also other metals that are used frequently as mirrors such as: Copper (Cu), Nickel (Ni), Platinum (Pt), and Rhodium (Rh). Dielectric films are deposited on metal mirror surfaces either to produce 'Protected Metal Mirror' or 'Enhanced Metal Mirror'. In the protected metal mirrors, the application of dielectric film is to protect the mirror surface from tarnishing whereas in the enhanced metal mirrors, dielectric film is used to enhance the reflectivity around the designed wavelength and also narrow the high reflectivity region. In both the cases selection of the appropriate thickness of the dielectric film is very important.

Protective layers not only need to have their thickness optimized, but their refractive index needs to be as low as possible for high broadband reflectivity. Therefore, if the only protective film alternative is one with a high index, care needs to be taken to be sure that the optical thickness is at the maximum reflectivity. If the optical thickness is mismatched, reflectivity will be sacrificed [Chainani 2002].

Bare metallic silver is poorly qualified as a reflective surface for two reasons: it adheres weakly to glass and its surface tarnishes badly when exposed to the atmosphere. For these reasons, silver requires extra care when used as a first surface reflective coating. Nickel / aluminium based electroplated silver mirrors of circular and square shape are coated with silicon based protective anti-tarnish film by Plasma Enhanced Chemical Vapor Deposition Method at FCIPT. Moreover, reflectivity measurement is done before and after the deposition process followed by a corrosion test of the film deposited mirror is done as per the ASTM standards. These 'anti-tarnish' film coated mirrors have also passed the environment tests successfully. Thin films with appropriate thickness were deposited on flat circular and square shaped Nickel / Aluminum based silver mirrors using Plasma Enhanced Chemical Vapor Deposition method in capacitively coupled (13.56 MHz) RF plasma. Deposition experiments were carried out using an organic precursor with Nitrogen gas. Thickness of the deposited film was few hundreds A, with good uniformity over the substrate area. Thickness of the deposited film was confirmed by the thickness vs. colour calibration, in visible range of electromagnetic spectrum on Silicon substrate under the identical experimental conditions.

Thin film photovoltaic modules are usually supported on a glass back sheet. The qualities of the glass replacement plastic back sheet are that it should be mechanically durable and resistant to moisture ingress. These sheets should pass the IEEE 1262 'damp heat test', in which the PV modules will be subjected to 85^{o}C and 85 per cent relative humidity. For this application insulating thin films deposited by reactive pulsed magnetron sputtering method have been developed by the National Renewable Energy Laboratory in US [Barber 2002].

Barrier films are also being evaluated for the storage of high pressure hydrogen in storage vessels made of fibre composites and polymeric liner materials. Preliminary results of 75 nm Titanium film deposited on PET liner show a barrier improvement factor over uncoated liners by a factor of 4 for Hydrogen and 33 for Helium [Moser 1998]. Metal barrier films appear to be superior to oxide or carbon films.

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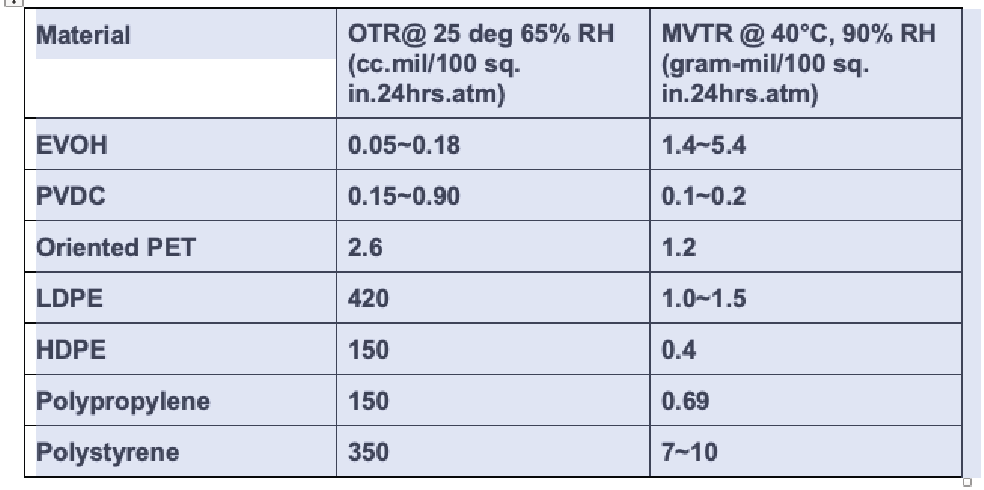
Table I

Food or beverage	**Maximum Oxygen Ingress permissible ppm (mass basis)**	**Maximum Water Gain or Loss% (mass basis)**
Canned milk, meats, fish and poultry	**1 – 5**	**3% loss**
Beer, ale, wine	**1 – 5**	**3% loss 20% CO_2 or SO_2 loss**
Canned vegetables, soups, Spaghetti, catsup, sauces	**1 – 5**	**3% loss**
Canned fruit	**5 – 15**	**3% loss**
Dried foods	**5 – 15**	**1 % gain**
Carbonated soft drinks	**10 – 40**	**3% loss**
Fruit juices, drinks	**10 – 40**	**3% loss**
Oils, shortening	**50 – 200**	**10% gain**
Salad dressings	**50 – 200**	**10% gain**
Peanut butter	**50 – 200**	**10% gain**
Jams, jellies, syrups, Pickles, olives vinegar	**50 – 200**	**3% loss**

Table II



Material	OTR@ 25 deg 65% RH (cc.mil/100 sq. in.24hrs.atm)	MVTR @ 40°C, 90% RH (gram-mil/100 sq. in.24hrs.atm)
EVOH	0.05~0.18	1.4~5.4
PVDC	0.15~0.90	0.1~0.2
Oriented PET	2.6	1.2
LDPE	420	1.0~1.5
HDPE	150	0.4
Polypropylene	150	0.69
Polystyrene	350	7~10

OTR = Oxygen Transmission Rate, or permeation rate of oxygen through material. MVTR = Moisture Vapor Transmission Rate, or permeation rate of water vapor through material

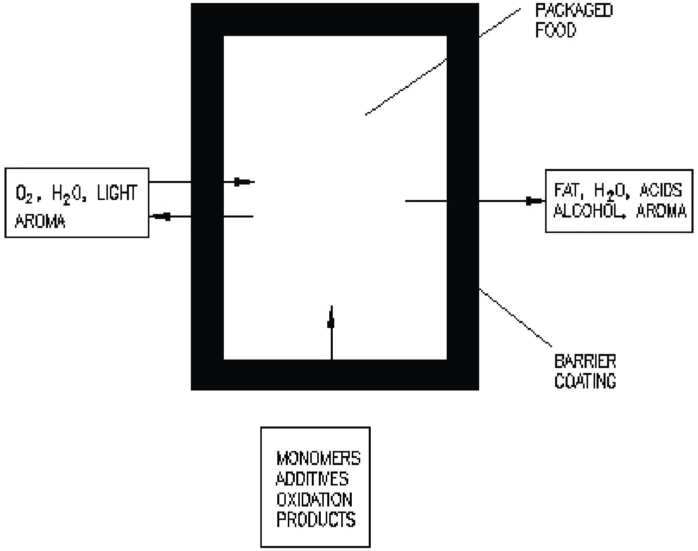


Fig. 11.1. Mechanisms leading to perishability of packaged food

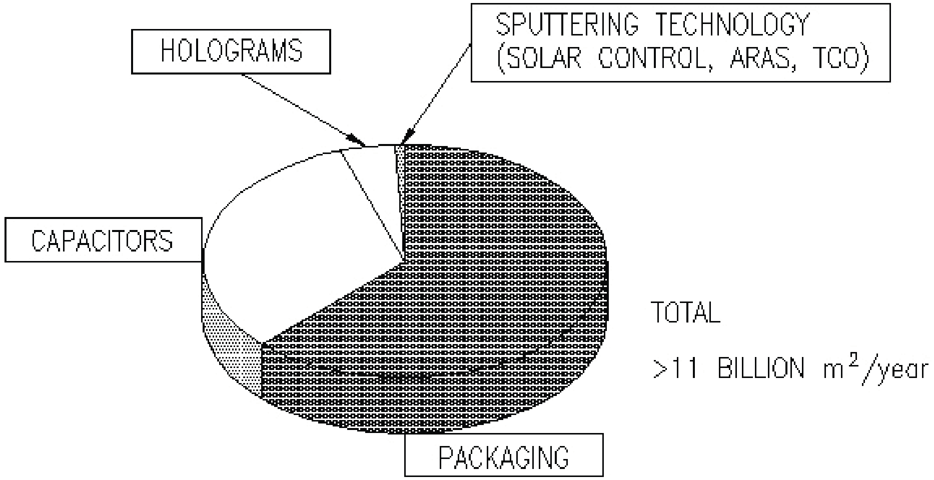


Fig. 11.2. Market share of barrier coating for food packaging (Figure courtesy of Dr. N. Schiller, Fraunhofer Institut fur Elektronenstrahl und Plasmatechnik, Dresden, Germany)

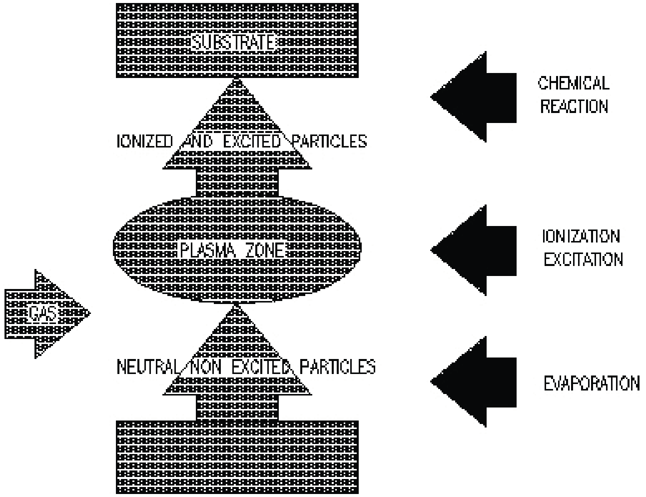


Fig. 11.3. Schematic diagram of reactive web coating using electron beam evaporation (Figure courtesy of Dr. N. Schiller, Fraunhofer Institut fur Elektronenstrahl und Plasmatechnik, Dresden, Germany)

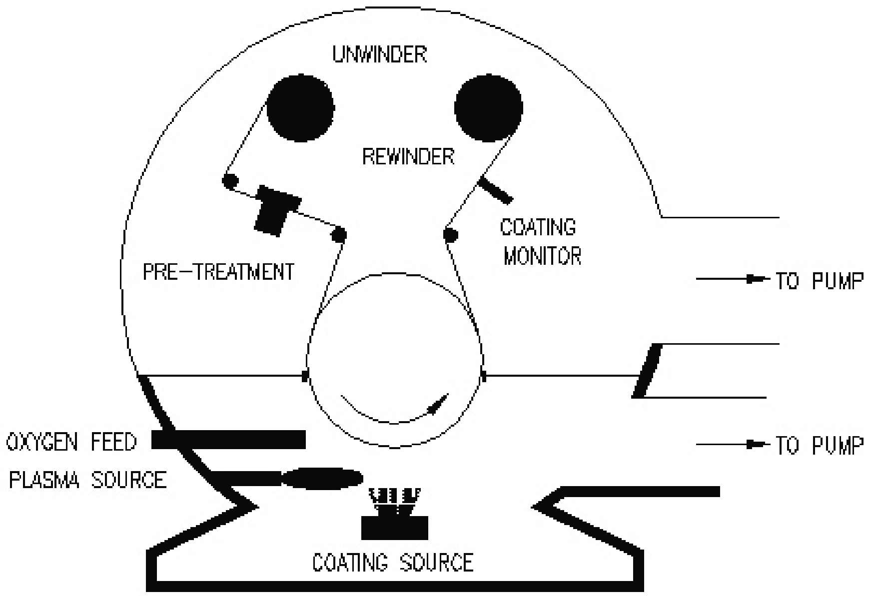


Fig. 11.4. Schematic of web coating by PVD process (Figure courtesy of Dr. N. Schiller, Fraunhofer Institut fur Elektronenstrahl und Plasmatechnik, Dresden, Germany)

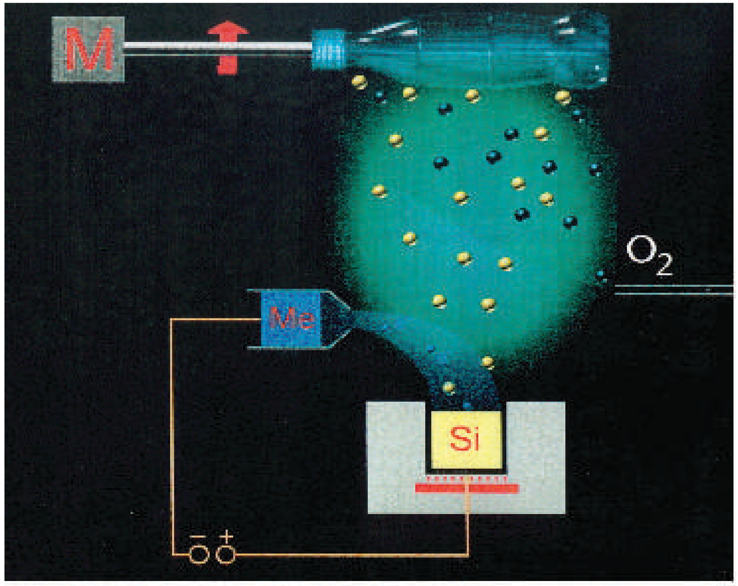


Fig. 11.5. The anodic vacuum arc technique for bottle coating (figure courtesy of Dr. H. Ehrich, University of Duisburg-Essen, Germany)

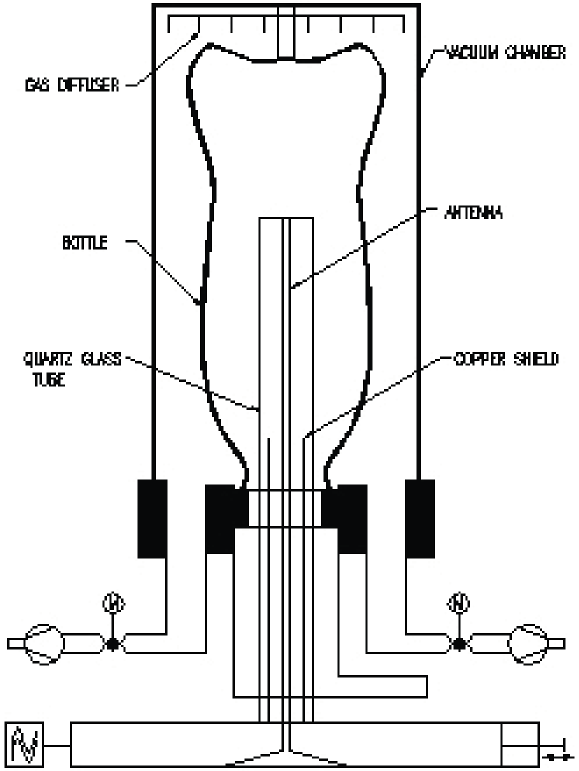


Fig. 11.6. Bottle coating with PECVD technique

12. Harvesting the Sun

Plasma Processing for the Solar Economy

The major issues in solar energy technology are: conversion of sunlight into electricity or heat, storage of energy in portable devices and conservation of energy. Plasma processing has become an essential tool for a variety of devices required in all the three components of solar economy. This chapter describes plasma techniques for manufacturing amorphous silicon devices and sun control coating of window glass.

The Solar Economy

Every year, the earth's surface receives about 10 times as much energy from sunlight as is contained in all known reserves of coal, oil, natural gas and uranium combined. Approximately 1 kW/m^2 of energy from sunlight is available on a typical land area of Earth. Taking seasonal variations into consideration the available energy per day is estimated as 4 kWh/m^2. Photovoltaic cells with an efficiency of 10 per cent can produce 0.4 kWh/ m^2/day. The per capita consumption of electricity in India is about 370 kWh annually or about 1 kWh daily. Assuming a three-fold increase in consumption, A billion of us would need 3 billion kWh of electricity per day. To produce this from solar power, a land area of 7000 square kilometres is needed. To put this requirement in perspective, India has a total coal bearing area of 44,000 square kilometres [NIC 2002].

Goldner [1995] has put forward quantitative arguments on the viability of the United States attaining a solar energy economy. The solar energy that the United States receives annually is 1000 times that of its electricity consumption. Electrochromic windows on buildings can conserve a significant fraction of energy since approximately 30 percent of the energy is wasted through windows. A photovoltaic generation station 20,000 square km in area at an average US location could generate all the electricity needed in the US (2.5 x 10^{12} kWh/yr.), assuming a system efficiency of 10 per cent, a balance-of-systems efficiency of 81 per cent and a system packing factor of 50 per cent. Thus although the solar resource is dispersed in area, it is ample to provide whatever amount of photovoltaic power is required.

Solar cells produce the cleanest electricity with no fuel consumption. They have long lifetimes, contain no moving parts, and require little maintenance. They are made from silicon, a material that makes 28 per cent of earth's crust. For an estimated 2 billion people who live world-wide in dispersed settlements not connected to power lines, solar energy is often the most affordable way to get electricity. Unfortunately, solar cells are far too expensive for widespread use. Despite the 40-fold price reduction, solar power is about three times too expensive for it to become a preferred power source.

Solar energy is very relevant to India. Close to 1,00,000 villages in India go without electricity. A majority of the villages being in remote areas, extension of grid power to these villages would involve heavy capital investments. The annual growth of demand at 8 per cent would require capacity additions of 20 Gigawatts over the next ten years. This presents a formidable challenge in terms of the organisational and financial capabilities needed in this sector.

The importance of renewable energy sources was recognised in India in the early 1970s. A significant effort has gone into the development and induction of a variety of renewable energy technologies - biomass, solar photovoltaics and wind energy - for use in different sectors of the economy. There are instruments to provide remunerative power purchase agreements and buy back of power to encourage exploitation of renewable energy. The Indian Renewable Energy Development Agency (IREDA) is the only Agency of its kind in the world dedicated to financing renewable energy projects. A broad goal of adding about 24,000 MW from renewable sources by the year 2012 is envisaged. The present annual production of solar cells in India is 47 MW. With over 75 companies manufacturing solar cells, modules and systems, India has now emerged as the second largest manufacturer of photovoltaic modules based on crystalline silicon technology. Photograph of a commercially manufactured photovoltaic module is shown in Fig. 12.1.

Photovoltaic Devices

Solar cells are based on the ability of semiconductors to convert sunlight directly into electricity. The scientific basis for this was the photogalvanic effect discovered by the French physicist, Edmond Becquerel in 1839. Driven by the need to power rural telephones Bell Laboratories made the first silicon solar cell with 6 % efficiency in 1954 [Chapin 1954]. The development was not put in commercial use because of the high cost. With the advent of the space programme, photovoltaic cells became the only viable power source for satellites.

Solar cells are fabricated from semiconductors, made from silicon doped with impurities. A p-n junction is formed when p and n type semiconductors are bonded. They have weakly bonded electrons in the valence band. When light with energy higher than what is called the band gap falls on a semiconductor, electron-hole pairs are created in sufficient quantities to lower the potential energy barrier at the junction, allowing current to flow and establish a voltage at the external terminals. Electrical current is taken from the device through a grid contact structure on the front that allows the sunlight to enter the solar cell, a contact on the back that completes the circuit, and an antireflection coating that minimises the amount of sunlight reflected back from the device. Figure 12.2 is a schematic depiction of a rudimentary solar cell that shows these important features.

Crystalline silicon is a semiconductor with an indirect gap. Its absorption in the spectral range of maximum solar power is relatively poor. Not all the photons are absorbed and turned into current; many deliver more energy than is required to make the electron-hole pair and about half of the photons have far too low an energy to make the pair. The losses from these processes are dissipated as heat and the maximum theoretical efficiency is around 25 per cent. Crystalline silicon cells hold the largest part of the market and consume 10 per cent of all the silicon processed into electronic devices. The modules have long lifetime (20 years or more) and their best production efficiency is approaching 18 per cent.

Thin Film Amorphous Silicon Devices

40 per cent of the cost of crystalline solar cells is due to the high purity silicon wafer [Ferrazza 1998]. The search for lowering the cost of photovoltaic materials has led to thin film solar cells. Materials such as hydrogenated amorphous silicon (a-Si:H), copper indium diselenide (CIS) and Cadmium Telluride (CdTe), are about 100 times more effective in absorbing the sun's radiation and can shrink the required thickness to 1 µm or less, requiring only 1/300 th of the material used in crystalline cells [Malsch 2003]. Conducting, dielectric and photoactive layer can be deposited on flat glass, stainless steel or polymer substrates [Barnett 1980]. However, of these, amorphous silicon technology has been the most commercially exploited.

Hydrogenated amorphous silicon (a-Si:H) has no long range structural order; an atom may be bonded to four neighbours, but not organised into a regular lattice. The short-range order gives it a band structure and the associated concepts of conduction and valence bands. With random orientations, in many cases one or more bonds go unconnected; the so-called dangling bonds can capture charge carriers and reduce conductivity. Atomic Hydrogen introduced from the Hydrogen and Silane plasma used for chemical vapour deposition of the film, ties up the dangling Silicon bonds. An important property of a-Si:H is its direct band gap, resulting in 100 times more efficient photon absorption than crystalline Si. The electro-optical properties are tuneable over a wide range by changing the Hydrogen content. The schematic diagram of a a-Si:H solar cell is given in Fig. 12.3a [van Swaij 2000]. This contains a p-type a-SiC:H layer, an intrinsic undoped a-Si:H layer and a n-type a-Si:H layer. Electron-hole pairs are generated in the intrinsic layer and drift under the action of the internal electric field to the electrodes. Because the intrinsic layer is sandwiched between n and p type layers, an electric field exists across the layer. The electron-hole pairs created by light falling on the intrinsic layer drift to the electrodes and constitute the current [Van Swaij 2000].

When light falls on amorphous Silicon, additional damage sites are created [Staebler 1977]. This distorts the electric field and reduces drift and thereby efficiency. The solution is a tandem or multijunction structure as shown in Fig.12.3b. Each component cell is thinner and less sensitive to light induced distortion of the electric field. The tandem configuration also allows each cell to be tailored to respond to different spectral ranges by changing the composition; for example by adding Germanium to form a-SiGe:H.

Polycrystalline thin-film cells comprise of many tiny crystalline grains of semiconductor materials. The materials used in polycrystalline thin-film cells have properties that are different from those of Silicon, so it has proven to be better to create the electric field with an interface between two different semiconductor materials. This type of interface is called a heterojunction in which the top layer is made of a different semiconductor material than the bottom semiconductor layer. The top layer, usually n type, is a window that allows almost all of the light through to the absorbing layer, usually p-type. An "ohmic contact" is often used to provide a good electrical connection to the substrate. Heterojunction solar cells incorporating p type a-Si and n type c-Si and with a junction with an intrinsic thin layer of a-Si with low defect density have reported intrinsic efficiencies of 21 per cent. These so-called HIT (Heterojunction with Intrinsic Thin layer) structures are simple in their structure and use simple low temperature plasma CVD process for fabrication. Research cells have shown better than 10 per cent efficiency. Such cells have higher conversion efficiencies at lower levels of light intensity, making them more competitive with conventional PV modules for use where there is haze or light cloud cover. The importance of the technology lies in its promise of low-cost processing for large-area modules, since most steps can be performed at atmospheric pressure. The cell is showing ever-greater performance and stability, both factors of concern to research and manufacturing groups. Even in its infancy the technology represents one area of thin films that is an alternative to conventional junction solar-cell approaches.

Copper indium diselenide (CIS) and cadmium telluride (CdTe) began to be explored for use in solar cells in the early 1970s. Their advantages include the possibility of engineering the desired optical response and control of electronic phenomena within the solar cell, and their high optical absorption (a direct-bandgap transition) that minimises absorber-layer thickness. They have stable electro-optical properties and both n- and p-type semiconductors are available. A greater emphasis has been on modifying the cadmium-sulphide CIS heterojunction and producing Gallium-containing alloy of CIS (CIGS). Research cells have demonstrated efficiencies as high as 18.8 per cent in this case. With a nearly ideal band gap of 1.44 eV, CdTe also has a very high absorptivity. At the heterojunction there forms an interfacial cadmium-sulphur-telluride layer, a graded alloy that may reduce the density of interface states and shunt paths. The potential problems in large scale exploitation of these devices are the toxicity of Cadmium and the high price of Indium.

III-V semiconductors such as gallium arsenide, gallium aluminum arsenide and gallium indium arsenide phosphide (GaAs, GaAlAs, and GaInAsP) have been combined in multiple junctions to reach high efficiencies. Cells in the 30-34 per cent efficiency range have been realised for these structures. Attention has of late centred on the two-terminal, two-junction tandem cell of GaInP on GaAs, with the best efficiency of 30.3 per cent under nonconcentrator conditions.

New thin film technologies in the horizon are dye-sensitised devices based on titanium dioxide discovered by Michael Gratzel in Switzerland's Ecole Polytechnique Fédérale de Lausanne. The titanium dioxide semiconductor used by the device has a bandgap in a range that is insensitive to the non-ultraviolet solar spectrum. To achieve a photo-response across the visible portion of the spectrum, the two steps of the photovoltaic process are separated. The oxide semiconductor is sensitised by a single layer of a photoactive dye that absorbs light across the width of the visible spectrum. Charge separation occurs by electron transfer from the photoexcited dye to the semiconductor substrate, in such a way that the dye molecule is left oxidised. The original ground state of the dye is restored by charge-transfer reactions with the electrolyte.

Plasma Processing of Thin Film Solar Devices

The major issues in solar energy technology are: conversion of sunlight into electricity or heat, storage of energy in portable devices and conservation of energy. Plasma processing has become an essential tool for a variety of devices required in all the three components of solar economy. In manufacturing amorphous silicon devices, the plasma route mediates deposition, etching and passivation. Window glass coating and manufacturing of thin film batteries use plasma assisted thin film coating processes.

The technique of plasma deposition of amorphous silicon thin films was discovered in 1965 [Sterling 1965, Chittick 1969]. Two crucial properties of the films are hydrogenation and doping with selected impurity atoms. Plasma processing with silane naturally incorporates Hydrogen into the film during its growth [Triska 1975]. The plasma deposition process can also be used for doping the semiconductor with Phosphorous and Boron by introducing phosphine and diborane into the processing gas stream [Spear 1975]. Both these paved the way for plasma processing to become the enabling technology for thin film solar devices.

Cold nonequilibrium plasmas with electron temperatures much higher than that of neutral species provides catalytic enhancement of chemical reactions, leading to plasma-chemical routes for synthesising films and coatings. In the PECVD technique, electrons gain energy from the electric fields and transfer it to the heavy particles. The energy distribution has to be such that the dissociation of heavy molecules, excitation and ionisation can proceed at the required rate. Amorphous silicon and passivating coatings like silicon nitrides are two such materials, which are of interest in the photovoltaic context.

The basic concept of the plasma deposition process can be illustrated in the planar diode system shown schematically in Fig. 12.4. RF power at 13.56 MHz is applied to two electrodes of unequal area. The electrode with smaller area acquires a large negative potential due to rectification of the RF voltage by the plasma sheath. The substrate for deposition is kept on the smaller electrode. Collision with energetic electrons dissociates silane introduced into the chamber into primarily SiH_2, SiH_3 and Si_2H_5. The radical SiH_3 has been considered for a log time to be the growth precursors, contributing to the film growth. Recent evidence suggests important role for Si atoms also. In many reactors SiH_2 is filtered out using a mesh above the cathode. The process allows specific compositions to be incorporated. To make p type material, diborane (B2H6) is added for Boron doping. Adding germane (GeH4) or methane (CH6) allows Germanium and Carbon to be incorporated.

However, diode RF plasma CVD is a slow process; deposition rates are typically 5 A/Sec. Improvements by adding magnetic confinement to the basic device have been developed. Faster deposition techniques are essential for large volume production. Using an expanding thermal plasma [Van Swaij 2000], high deposition rates of the order of 100 A/Sec has been demonstrated [Fig. 12.5]. This is a remote plasma technique, where the plasma produced using an arc discharge diffuses into the deposition chamber. The feed gases are introduced into the expanding plasma jet and undergo dissociation prior to deposition. Photograph of the expanding plasma system is given in Fig. 12.6.

Very high frequency (VHF) discharges have been found to increase the deposition rate [Curtins 1987] to typically 20A/sec, much larger than what is obtained in RF discharges. As the frequency increases the sheath thickness deceases (d~ $f^{-0.7}$) and hence the power dissipated in the bulk increases in relation with the power dissipated in the sheath. The total impedance of the VHF plasma is substantially lower than that of RF plasmas. The reduced sheath voltage drops also helps to decrease the ion energies, reducing the potential for defect formation in the deposited film. The increased electron density due to the increased power absorption enhances the radical densities as well as the formation of Silicon precursors, aiding film deposition. It has been postulated that the enhance of low energy ion flux to the surface helps in the formation of microcrystalline Silicon films (μc-Si:H), which are more efficient in absorbing photons [Kroll 1995].

To meet large-scale commercial demand, the thin film process technology has to graduate from the batch processing technique to continuous processing. Industrial systems use multiple chambers where a specific deposition process is done in one chamber and the substrate is moved under vacuum to another chamber for another process. Both cluster configurations and in-line configurations are common. This not only reduces contamination, but is also ideal for multilayer devices.

Roll to roll deposition technology is being implemented commercially by Unisolar, Canon, Sanyo and Fuji among others. The Helianthos project [Middleman 1998] with industry and institution partners has set a cost objective of 0.5 Euro/peak watt and a production level of 1 million square metres/year.

A continuous moving temporary substrate such as a metal foil is used to deposit a textured transparent conductive oxide layer. A multijunction p-i-n-p-i-n structure is then deposited over this. After laser patterning, the back contact is deposited. A final patterning completes the series connection of individual strips and subcells. The interconnected cells are laminated with a permanent carrier foil. Finally the temporary substrate is etched away and a final encapsulation is deposited.

Sun Control Glasses

Glass has been an architectural material for centuries. Glass is chemically inert, stable against environmental attacks and can be manufactured in large volumes at very low cost. Its high transparency in the visible spectrum permits a neutral colour. It is now used extensively in buildings for cladding and windows, not to mention a myriad of other applications.

From the perspective of energy conservation, glass, however, has many drawbacks. Solar radiation useful for lighting falls between wavelengths 400 nm and 700 nm, and half of the sun's blackbody radiation is contained below ~2500 nm [Fig. 12.7]. A quarter inch thick plate glass is essentially transparent to the entire solar spectrum except the short wave ultra-violet. Window glass transmits wavelengths between ~350 nm and 2500 nm with an efficiency near 80 per cent. It is less transparent, however, to wavelengths over about 3 microns and opaque to wavelengths over 4.5 microns. This means that solar radiation can pass through glass to heat surfaces inside a building, but the glass absorbs longer wavelength radiation from objects within causing the glass temperature to rise. This accounts for the "greenhouse effect" of trapping heat within glass enclosures. For internally heated buildings, the high emissivity of 0.85 meaning low reflection in infrared causes undesirable heat loss, estimated at 5 per cent of internal energy for a typical house in the western countries. For commercial and residential applications, maximisation of solar illumination is required with simultaneous control of internal heating and cooling. Manufacturers represent the energy efficiency of a windows in terms of their R (resistance to heat flow) value. Simple glass has an R-value of 0.85. Today’s super windows have an R-value in the range of 7.

Selective thin film coating technology, developed in the early 1980s, is being increasingly applied to the problem of controlling and moderating radiant energy loss through windows. The coatings that satisfy this need can be deposited directly on window glass. Sputter deposition is the most common technique and the most economical for coating large rolls of polymer films and glass panes. Copper, Gold, Silver, and TiN are common materials that, in thin film form, transmit visible and reflect near to mid-infrared wavelengths.

Conductive coatings like Indium Tin Oxide (ITO) or doped SnO_2 or or that of a metal have low emissivity. The deposited film layer must contain a high density of charge carriers for good heat conduction. These carriers are free electron and Oxygen vacancies, whose excessive population produces absorption. Doped oxide semiconductors having large bandgap, for example, In_2O_3: Sn (ITO), have the property of transmitting below ~1000 nm and reflecting above ~2000 nm. Thus, the major heating wavelengths of the sun are admitted, and the radiant heat of the interior is prevented from escaping. With ITO coating on window glass, light and some solar heating is admitted, but radiation from warm objects at 300 K is prevented from escaping. This serves to reduce heating requirements in cold weather. ITO films behave as metals to long wavelength light because of the presence of a plasma wavelength above 1 µm. At longer wavelengths, the film becomes reflecting, and the IR reflectance is related to the sheet resistance of the film.

The metal layer is sandwiched between dielectric layers to increase visible transmission and to protect the metal from abrasion and corrosive degradation. Metal layer thickness is below ~100 Å, and the deposition method is important in determining the amount of coalescence that occurs at this thickness. A greater degree of coalescence results in higher reflection and therefore lowers transmission. A precursor layer is deposited first, which helps adhesion and controls the amount of metal agglomeration.

Spectrally selective coatings are more complex than low-e coatings. They are designed to filter out 40-70 per cent of the heat normally transmitted through glass, while allowing light to be transmitted [NREL 1994]. High index quarter-wave dielectric films such as TiO_2, Bi_2O_3, ZnO, etc. with thickness one quarter of visible wavelengths are used to enhance transmission of the metals Au, Ag, or Cu without reducing the reflection of IR energy. The design is: dielectric-metal-dielectric (D-M-D). Designs based on a Fabry-Perot cavity consist of D-M-DD-M-D, where DD represents a half-wave spacer. A typical result for the design 300 Å TiO_2 - 130 Å Ag -300 Å TiO_2 is ~80 per cent transmission in the visible and 80 per cent reflection from 2000 nm and above.

Coatings for heat generation are characterised by high absorption of solar energy and low emittance at longer wavelengths. The coatings might consist of a deposited cermet layer, which contains absorbing species in a dielectric matrix, or single or multiple layer designs. An example of the cermet approach is a nickel-silicon oxide black material that can be evaporated. Another is Cr - Cr_2O_3. One design consists of a thin layer of Ti immersed between TiO_2 layers. Multi-layer structures such as Al_2O_3 - Mo - Al_2O_3 have been developed for stability at the high temperatures generated. Absorbing materials with intrinsic selectivity such as ZrB_2 are also used. Ge and Si layers on Aluminum absorb short wavelengths and reflect above 2000 nm and 1000 nm respectively.

Radiative cooling coatings depend on the property of some materials to absorb energy in the thermal IR, i.e., near 10 µm, near the centre of the 300 K blackbody emission curve. They emit this energy efficiently. Silicon oxides and oxynitrides are useful for this application.

Coatings which exhibit variable optical and thermal properties in response to light, the so-called smart windows, are becoming important both from architectural and energy conservation point of view. Such devices are based on the rendition of colouration to solid films to produce variable light transmittivity. A schematic diagram of such a device is given in Fig.12.8. The central part is an electrolyte, which allows transport of ions through it. On both sides are transparent electrodes made typically of indium tin oxide. An electrochromic material such as tungsten oxide is coated on inner side of one electrode while the other electrode is coated with nickel oxide. On application of a voltage across the device, cations and electrons can be injected into the electrochromic layer, causing colouration. The device remembers the coloured state even after the removal of the voltage. However, an application of a reverse voltage will reverse the process and remove colouration. Thus the process during bleaching may be viewed as a chemical reduction occurring at the positive electrode (nickel oxide) and oxidation occurring at the negative electrode (tungsten oxide).

The external circuit can also be used as a control device: The disconnection of the circuit will cause the window to remain in its current state regardless of the presence or absence of sunlight. In addition, an external voltage can be applied to the device through this circuit to drive the device to either the bleached or coloured state.

The transparent electrodes used in electrochromic windows are indium tin oxide (ITO) and tin oxide doped with Fluorine (FTO) or Antimony (ATO) [Radhakrishnan 1997]. These can be deposited by sputtering. Thin gold coatings also have been used as conducting coating. Many cathode and anode materials have been developed [Agarwal 1993]. However, Tungsten oxide deposited by sputtering and other methods seem to be the most popular cathode material. Large area coating with stable performance and colour contrast ration of 10:1 has been developed [Cronin 1999]. The colour changes from transparent to deep blue. Dyed colour can be controlled by addition of other oxides or metals (for example gold gives a red colour) [Sichel 1978]. Nickel hydroxyoxide is a preferred anode material, which becomes black when oxidised. The critical component in the electrochromic device is the electrolyte, preferred in solid thin film coating to match the large area coverage requirement. Many inorganic sputter deposited films have been developed as the electrolyte [Monk 1995].

A second requirement of the solar energy economy is efficient storage of electricity to take care of the diurnal variability inherent to solar energy generation. Recent results for completely inorganic, monolithic, single cell thin film batteries prepared by a number of laboratories look promising. The Eveready battery company reported that their TiS_2 cells have been reversibly deep cycled for more than 20,000 times with negligible change in the charging-discharging characteristics. The Tufts University group has been investigating Lithium ion battery cells that use Carbon films as anode.

It is conceivable that thin film batteries employing a cathode composed of one of the transition metal oxides and a carbon anode could have energy densities approaching 500 Wh/kg.

The Future of photovoltaics

Solar energy currently makes up less than 1 per cent of global energy output: there is a total of about 800 megawatts of solar power capacity in place around the world. Worldwide sale of photovoltaic systems reached 400 MW in 2001 [Jager Waldau 2002] and to 560 MW in 2002 [Maycock 2003]. With a growth at 15-30 percent per year, solar energy has become world's fastest-growing energy source. A US industry roadmap anticipates that photovoltaics would supply 15 percent of the added capacity needed each year in the early 2020s. The United States and the European Union have set a goal to install one million solar rooftop systems by 2010. Large installations like the solar roofs for the Olympic stadium in Atlanta and a skyscraper in Times Square are making photovoltaics quite visible. Japan has set aside 16 billion Yen annually to install 5 GW by 2010. From 1994, New Energy Foundation in Japan has been subsidising photovoltaic power generation systems used in individual residential homes. Japan’s rooftop solar programme installed solar cells, which began in 1994, have installed 280 MW on 77,000 by 2001 [Maycock 2003].

For photovoltaics to be widely used, the system price per kWh produced must be such that the electricity cost taking into account the investment in installation must be competitive with those of conventional forms of electricity. The breakeven figure is considered to be \$ 500/ m^2 for a 10 per cent efficiency unit operating for 30 years. In the US, the average price for electricity is 6-7 cents per kilowatt-hour. Today photovoltaics generate electricity at 20-30 cents per kilowatt-hour. Therefore the costs must come down by about a factor of 4 to compete in the bulk electricity market. Goals for truly inexpensive PV systems are pegged at an ambitious 15 per cent efficiency, 30 year life and \$ 75 per peak Watt [Zweibel 1995]

Denis Hayes of the Earth Day fame advocates that a federal program to spend \$8 billion over the next four years could make solar cells commercially viable for a significant portion of new electrical applications world-wide. This is inspired by the history of Silicon chips. In the 1960s, computer chips were very expensive. Massive government purchases by the Defence Department and NASA quickly led to design innovations, efficient mass production and low prices. Today, millions of people have more computational power available in their PCs than NASA had for the entire Apollo space program in the 1960s. The same strategy could work for solar cells, too.

The drive for cheaper and more efficient solar cells is continuously generating new concepts and techniques. The possibility of varying the bandgap in polycrystalline alloys like $Cu(InGa)\ Se_2$, $Cu(InAl)\ Se_2$ or CdTe is being explored to produce clever configurations. A tandem device with 1.6-1.8 eV bandgap top cell and 1.0-1.2 eV bandgap bottom cell has a theoretical efficiency of 30 per cent. Improving the quality of these alloys or development of new alloys are priorities in the multijunction device roadmap [Hegedus 2003]. Other attempts to fully utilise the solar spectrum has led to the intermediate band concept [Luque 1997] where the transfer of valence electrons to the conduction band is a two-step process absorbing two photons. Nanotechnology [Marti 2000] is enabling the realisation of this concept through quantum effects in quantum dots.

A number of factors influence photovoltaic energy costs. Foremost are the module efficiency, lifetime and cost per unit area. It is clear that lower-efficiency modules have to cost less than higher-efficiency modules to produce the same cost of electricity. Hence there is a premium on higher efficiency. Efficiency can be traded off against infrastructure costs (such as land, wire and support structure) to achieve the same cost of electricity.

A survey of the overall market and its growth is quite educative [Jager-Waldau 2003]. The growth of solar energy market in the period 1988-2001 is shown in [Fig. 12.9]. Within the period 1994-2002, Japan has assumed a position of world leadership in solar energy systems in both production and usage. The 42 per cent market share will rise to 51 per cent with the new industry initiatives being put into implementation in Japan. Sharp, one of the major manufacturers announced reaching a production figure of 148 MW [Sharp 2002]. Japan sees photovoltaics as a key 21st century industry. The 'old economy ' giants like Mitsubishi and Sumitomo are seen moving into the solar energy business consequently.

Compared to Japan, Europe and US have shown more modest growth. New initiatives in Italy (10,000 roofs programme) and United Kingdom (Major photovoltaic generation project) are indicative of growth. A US Roadmap for photovoltaics indicates its commitment to regain the leadership position

As the cost of photovoltaic systems declines, the options for cost-effective applications increase. The ultimate application, bulk electrical power generation is expected to occur within the next 10 to 20 years, when photovoltaics decline in price below about 10 cents per kilowatt-hour. Various utility niche markets are expected to grow before these large-power markets do. The cumulative world market is shown in Fig. 12.10.

Market growth will be tied to the continuing decline in photovoltaic costs relative to conventional supplies. The industry will need to build larger, more cost-effective production plants that take advantage of available economies of scale. Investment in these new, large plants will require identification of sustainable markets. Many high-value applications taken together, including international rural electrification projects could provide the necessary market pull.

The electric utilities in the US will require extensive field experience, operation and maintenance data, as well as reliability data with photovoltaic systems before they will commit to large investments in power plants. The process of obtaining such data has begun at the Photovoltaics for Utility-Scale Applications (PVUSA) project in Davis, California, and other cities. Through this large, evolving utility-connected photovoltaic demonstration project a national public-private partnership is assessing and demonstrating the viability of utility-scale photovoltaic generating systems.

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1201 Fig. 12.1. Photograph of solar photovoltaic panels

Fig. 12.1. Photograph of solar photovoltaic panels (courtesy Tata BP Solar, India)

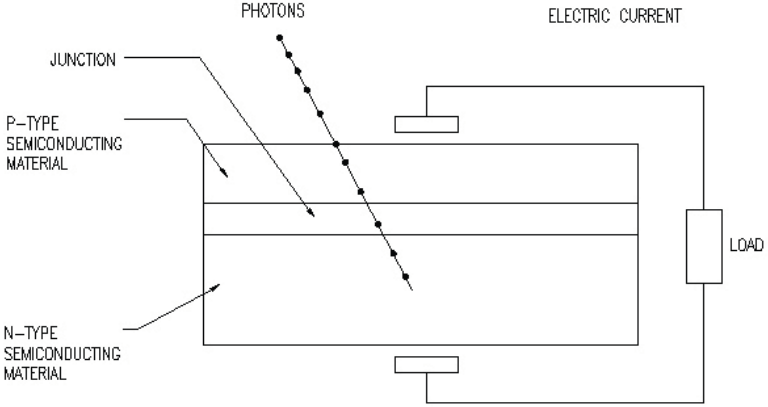

Fig. 12.2. Schematic diagram of operation of a solar cell

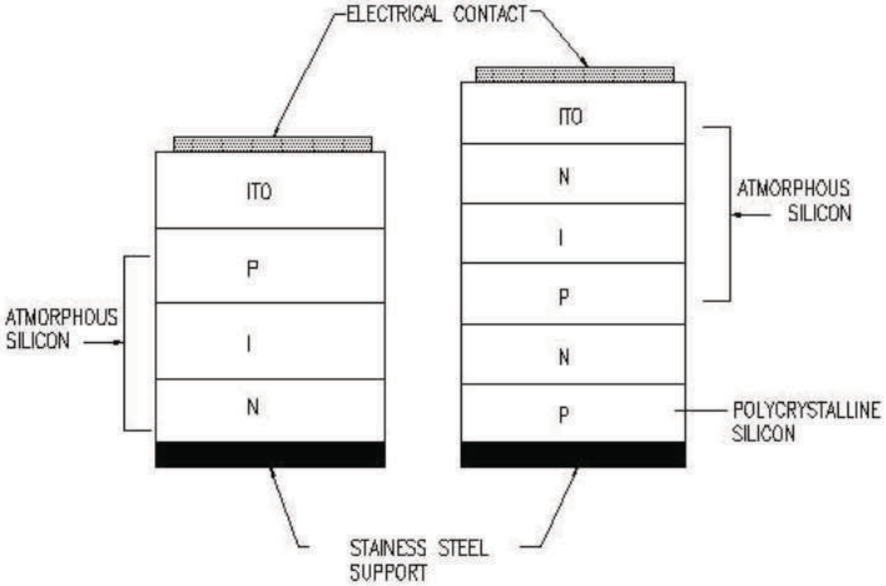

Fig. 12.3. Schematic diagram of (a) a-Si:H solar cell (b) multi junction solar cell

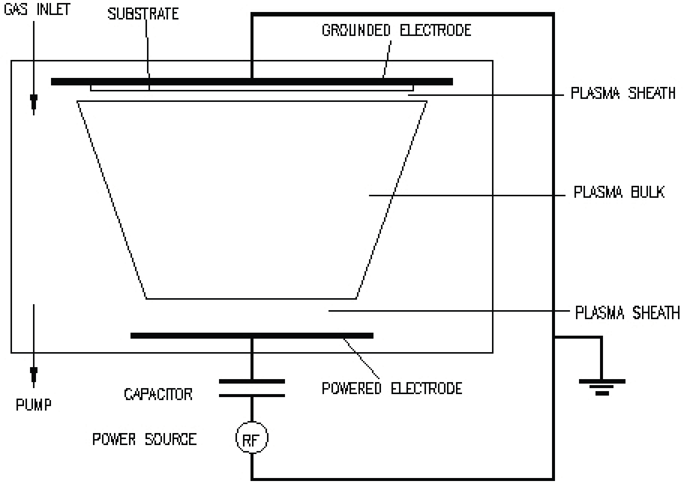

Fig. 12.4. The basic concept of the plasma deposition process using a planar diode system

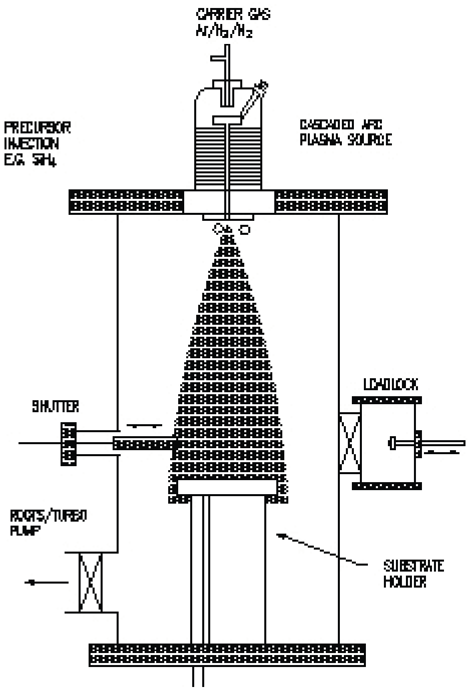

Fig. 12.5. Schematic diagram of an expanding thermal plasma system for fast deposition of silicon films (figure courtesy of Prof. M. C. M. Van Sanden, Eindhoven University of Technology, the Netherlands)

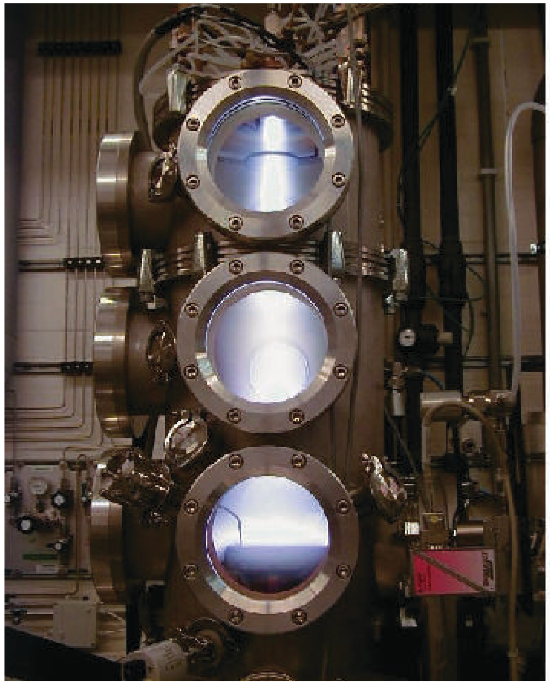

Fig. 12.6. Photograph of an expanding thermal plasma system (figure courtesy of Prof. M. C. M. Van Sanden, Eindhoven University of Technology, the Netherlands)

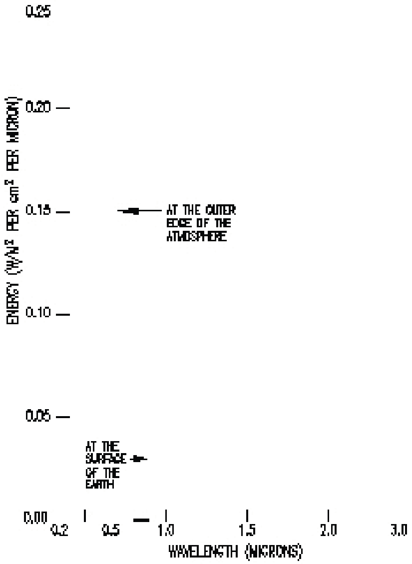

Fig. 12.7. Solar radiation useful for lighting falls between wavelengths 400 nm and 700 nm, and half of the sun's blackbody radiation is contained below ~2500 nm

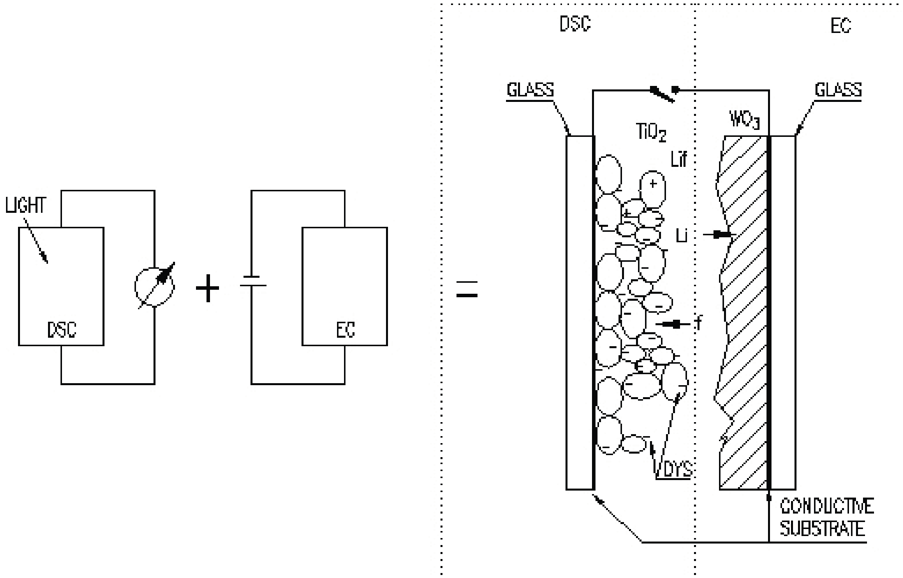

Fig. 12.8. Functioning of a electrochromic window

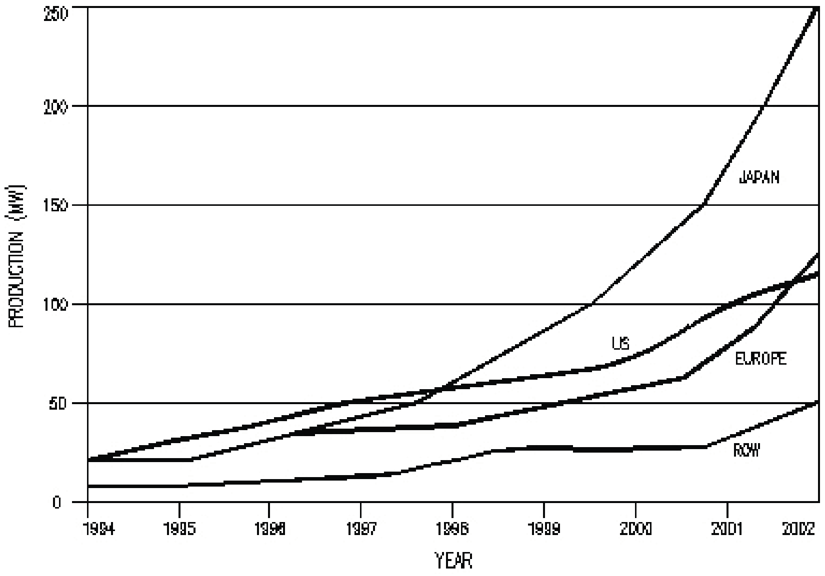

Fig. 12.9. Region wise growth of photovoltaic market (figure courtesy Dr. Paul Maycock, PV News)

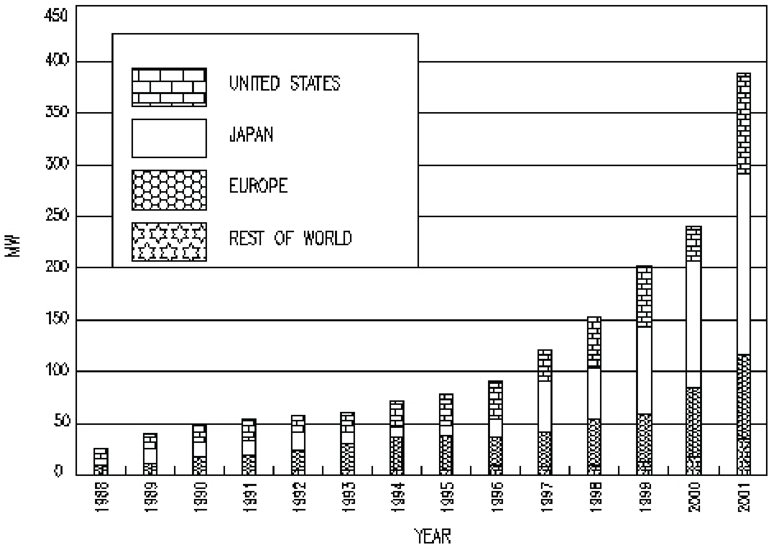

Fig. 12.10. Cumulative growth of the photovoltaic market (figure courtesy Dr. Paul Maycock, PV News)

13. Inside Intel

Microelectronic Device Processing

The convergence in information, communication and entertainment is a major outcome of the microelectronic revolution. The miniaturisation in electronic is made possible by the atomic scale manufacturing using plasma processing, which entered microelectronic manufacturing in the 1970's. This chapter explores the ways in which the core processes like etching, deposition and doping in microelectronics are enabled by plasma techniques.

Evolution of Microelectronics

In the early 1947, scientists John Bardeen, Walter Brattain and William Shockley at the Bell Telephone Laboratories discovered that Germanium crystals with some impurity added had the property of regulating electric currents [Brinkman 1997]. Thus was born the transistor, which was immediately seen as a cheap replacement for the expensive and bulky vacuum tubes. The original invention was called a point contact transistor, which soon gave way to the junction transistor, smaller in dimensions and more amenable to mass manufacturing. This indeed was symbolic of the revolution that would come in electronics: the ability for astonishing scales of miniaturisation while retaining the basic phenomenology. The fundamental operation remains unchanged even when the device size has shrunk more than 10,000 times It has been estimated that producing a transistor now is cheaper than printing a character in a newspaper.

The next step was the fabrication of a number of transistors on a single wafer. The devices however were still discrete, and they were individually packaged in tiny cans. An early form of integrated circuits had components like diodes, transistors, resistors, and capacitors formed on the same chip, but hand-wired into a circuit.

The year 1959 saw the new process called planar technology conceived by Jack Kilby of Texas Instruments, in which various layers were diffused onto the surface of a Silicon wafer to make a transistor, leaving a layer of protective oxide on the junctions. Metal interconnections were evaporated onto the flat transistor surface replacing hand wiring. This new process made commercial production of integrated circuits possible. The next breakthrough was to use Silicon as the capacitor in the circuit. If all parts of the circuit are made of one material, they can be manufactured in a single step from a monolithic block of material.

Further progress was in miniaturisation. Today's microelectronic devices are complex structures formed on the surface of semiconductor wafers. Millions of transistors, capacitors, resistors and diodes are microscopically wired together to form circuits in approximately one square cm. Area. The trend towards larger wafers and smaller transistors reflects the economy of scale in microprocessor manufacturing. The closer packing of a larger number of transistors makes the larger chips faster than smaller ones. By the end of the 1960s, nearly 90 per cent of all the components manufactured used integrated circuits.

Gordon Moore, research director of Fairchild Semiconductor who later founded Intel Corporation predicted that the number of transistors on a chip would double every year. This, shown in fig.13.1 is now known as Moore's law [Moore 1965]. Between 1970 and 2000, the number of transistors per chip increased by a factor of 10,000, with a doubling time of two years [Quirk 2001]. There is concomitant decrease in minimum device dimensions. To put 5 million transistors on a Pentium chip, the individual elements have to be below 0.5-micron size. Intel's Pentium III contains 28 million transistors. Ultralarge-scale integrated semiconductor circuits contain structures having minimum pattern widths of 0.25 μm and less. The processing complexity has also scaled inversely with the characteristic dimensions, going from the 1-μm minimum pattern widths of the early 1980s to the 0.25-μm (and lower) level of ULSI circuits.

The revolution of consumer electronics, communications infrastructure, and a host of portable business/personal devices are driving the evolution of microelectronic device technology towards integration of entire systems onto a single chip. The dominance of the PC industry as a driver for semiconductor technology is being taken over by these emerging markets. Reduced power consumption as well as price is the major attraction. Fewer components can mean improved reliability, simpler logistics, and lower assembly costs.

However, the technological barriers are many. More process steps result in decreased yield as well as design flexibility. If both analogue (bipolar) and digital (CMOS) circuits are needed on the same IC, different process technologies are required. Materials with good heat transfer properties are being found for power devices, and processing technology is being advanced so that different power applications can be designed onto a single chip. Work on package designs should enable use of proven PCB assembly methods.

Miniaturised module assemblies using wafer-scale components are being developed for attachment during final PCB assembly. A new generation of surface-mount device placers will be required to assemble these modules, offering high placement accuracy (5-10µm) and low contamination. These modules will be suited for new placement methods, possibly using ceramic or flexible substrates.

Two-dimensional miniaturisation is reaching its limits in cost and complexity. Further development will make forays into three-dimensional stacked chips. The ultrahigh scale density results in increased speed and power by factors of hundreds to thousands [Suhir 2000]. Forming interconnects within the vertical stack is the primary technical obstacle to mass production of 3-D vertically integrated packages. This has limited 3-D packaging to low-volume, very specialised uses, such as military and medical applications, and supercomputers.

Plasma Processing in Microelectronics

Plasma processing became the critical enabling tool in IC manufacturing in the late 1970's and early 1980's and have become the essential tool in IC manufacturing. At present, 30 per cent of the processes are plasma based [Proud 1991]. $ 17.6 billion worth of plasma reactors were sold in 1999, manufacturing $ 245 billion worth of chips. The market is projected to grow to $ 33 billion by 2004 [Kharif 2001]. Plasma processing now covers the manufacture of DRAMS, SRAIMS, MODFETS, Thin Dielectric Gate Oxides and new materials for optoelectronics: Silicon Germanium alloys, High temperature electronic materials like diamond and diamond like Carbon films, silicon carbide, cubic boron nitride and many more materials and devices.

The starting material for semiconductor processing is crystalline or amorphous Silicon film. Plasma CVD is the major technology for making a-Si: H. In plasma CVD, the plasma medium generates the species that subsequently react and deposit on substrate surfaces. Besides enabling production of reactive species at much lower processing temperatures compared to conventional CVD processing, the ion bombardment can be used to modify film characteristics. The precursor film deposition in plasma CVD is SiH_4, diluted in an inert gas. The resultant material is hydrogenated amorphous silicon.

1. Deposition takes place in four major steps:
2. Electron-impact reactions between electron and reactant gases form ions and radicals
3. Reactive species are transported from the plasma to the substrate surface
4. Absorption and/or reaction of reactive species onto the substrate surface
5. The reactive species and/or reaction products incorporate into the deposited films

High density CVD processing usually involves simultaneous deposition and etching. The three principal mechanisms are ion-assisted plasma deposition, Argon sputtering, and redeposition of the sputtered material. In HDP CVD, a high-density plasma source [such as inductively coupled plasma (ICP), electron cyclotron resonance (ECR), or helicon] excites a gas mixture that includes Silane, Oxygen, and Argon. The substrate is negatively biased to attract energetic positive ions toward the wafer surface, where Oxygen reacts with Silane to deposit silicon oxide, and Argon removes the silicon oxide by sputtering.

Two types of circuit patterning techniques are employed in semiconductor fabrication, which are complementary to each other [Rossnagel 1999]. The choices are dielectric imprint on metal or metal inlay on dielectrics schematically shown in Fig.13.2. The first, known as RIE patterning has the following steps:

1. Deposit a uniform metal layer over the wafer surface
2. Coat the surface with a photosensitive polymer called photoresist
3. Project a pattern optically on to the photoresist to alter its solubility
4. Create a mask by dissolving the soluble portion by reactive etching
5. Etch the metal not protected by the mask
6. Remove the mask by plasma stripping
7. Passivate the surface by depositing silicon dioxide or silicon nitride

The second class of patterning technique is inspired by the ancient jewellery-inlay process [Kaanta 1991] and is known as damascene processing. This starts with a planar dielectric layer on which interconnecting trenches are etched. The depressions are filled using metal deposition process forming an embedded line in a planar surface. This process is repeated by depositing another insulating layer to form the basis for the next layer of metal film.

Etching in Semiconductor Manufacturing

The first step in making integrated circuits is to project a circuit pattern from a mask. Ultraviolet light exposes a photosensitive polymer photoresist, which is then developed by removing the irradiated regions. Once the pattern is defined in the photoresist, etching transforms the pattern onto the underlying film, such as polycrystalline Silicon to make transistor gates, Aluminum or Copper to make interconnections between devices or silicon dioxide to isolate interconnection paths. The aim of etching is to transfer lithographic features to the substrate with high fidelity. Etch selectivity to different films is also essential. Very high selectivity to the underlay is required, for example, to avoid shorting from one conducting metallization level to another. If the etching is directional, the lithographic pattern can be transferred with high fidelity to the underlying material.

Plasma etching, introduced in the 1970s [Manos 1989], uses plasma to convert molecular gases into chemically reactive species. These reactive species combine chemically with solid materials to form volatile compounds, which are removed by the vacuum pumping system. Four types of materials have to be etched: doped or undoped Silicon, dielectrics such as SiO_2 or SiN, metals (usually Aluminium, Tungsten or Copper) and photoresist. The chemistry is different for each material. Plasma etching should have anisotropy to produce sharply etched profiles, selectivity for material specificity and uniformity. The process is a combination of physical etching due to ions and chemical etching due to radicals. Plasma etching has grown from the use of relatively simple, parallel-plate diodes to million-dollar cluster chambers with multiple-frequency generators, electrostatic chucks, externally controlled wall temperatures, and a variety of process-control sensors designed specifically for one type of film.

The dielectrics to be etched are silicon dioxide and silicon nitride. Dielectrics have tenacious bonds and hence the etching uses highly reactive Fluorine plasma made from fluorocarbon gases such as CF_4, $C4F_8$ etc. The complex plasma chemistry of these gases also results in polymer deposition. Energetic ions are used to etch away this material. As the lateral trench dimensions shrink, the energetic ion and radical flux to the bottom of these features is reduced owing to collisions with the sidewalls and with other species. As etch products accumulate and polymerise within the trench, they cause distortion of the feature [Buie 1996].

A major problem in etching is the charging of dielectric surfaces. Positive ions are accelerated from the plasma and travel deep into the bottom of the trenches. In contrast, electrons diffuse isotropically to the wafer surface and are absorbed at the upper surface of the IC features present on the wafer. This causes a potential difference to develop between different parts of the structure. Thus, the low-energy ions are retarded or reflected to the walls, while the electrons are pulled down into the structure. This causes features to be charged differentially from top to bottom. Also, the reduced ion current and energy of the ions that reach the bottom surfaces contribute an aspect-ratio-dependent phenomenon known as "RIE lag" [Fujiwara 1997], in which etching rate is proportional to the dimensions of the structure.

Process economics demand large cross section plasmas for treating large-scale integrated electronics systems. Density, temperature and potential uniformity of 3 % over the plasma cross-section is the industry benchmark. To increase the etch rate, particle density of 10^{12} /cc at a few millitorr is desired with controllable ion energy, orbits and electron energy distribution function. The etcher also should be free from contamination from sputtered or plasma-chemically synthesized microscopic dust particles.

The surface loaded parallel plate radiofrequency capacitive diode etcher [Reinberg 1973] is illustrated in Fig.13.3. Molecular gases flowing into the chamber are dissociated by the application of RF power. The predominant chemical effect on the wafer is from chemically reactive radicals created by electron impact dissociation. The mean free path of electrons has to be smaller than the gap between electrodes for plasma sustenance, which makes the sheath collisional. The wafer is kept on the powered electrode and acquires a negative bias by sheath rectification. The negative bias accelerates ions to the wafer, which arrive with a flux and energy, which are, inter-related [Lieberman 1994]. This limitation can be removed if the top and bottom electrodes are powered at different frequencies. If the frequency on the top electrode is greater than the plasma ion frequency, density and hence the ion flux will be controlled by the power on this electrode. The voltage of the lower electrode will determine ion energy.

The capacitive etcher seems to have reached its density and power limits. The high sheath voltage produces undesirable effects like the junction damage, macroparticle production etc. For electronegative gases this is even worse since the volume recombination increases in the bulk plasma. The plasmas used for processing new devices have to be of higher density to allow smaller sheath sizes, provide anisotropy in smaller scale lengths, have higher uniformity to allow uniformity of processing on larger dimensions, lower electron temperatures to reduce electric potentials and damage of dielectric films, etc. The three competing high-density plasma sources presently available are the electron cyclotron resonance source (ECR), inductively coupled plasma (ICP) and the helicon plasma source [Fig. 13.4- 13.6].

The ECR [Stevens 1992] source utilises the resonant absorption of electromagnetic waves at the electron cyclotron frequency to couple power to the electrons. With inexpensive magnetron sources available at 2.45 GHz, resonance occurs at 875 Gauss, a field strength easily achieved by electromagnets or permanent magnets. The resonant enhancement of power transfer can be by a factor of 10^5 at an operating pressure of 10 mTorr, which reflects itself in the enhanced density [Hopwood 2003]. ECR sources produce plasmas at densities of the order of 10^{11}-10^{12}/cm^3, roughly 10-100 times higher than the RF diode density. This source has been commercialised by Hitachi and Leybolds [Popov 1994].

The success of the ECR source motivated the development of inductive coupled plasma sources, whose basic principle dates back to Hittorf in 1884 [MacKinnon 1929]. In an ICP reactor [Marks 1992], an electric field is induced in a low pressure gas by the transformer action of a coil wound outside dielectric walls. The induced RF electric field accelerates electrons, which forms the plasma. The direction of the current in the plasma is opposite to that of the coil currents, which are by design parallel to the reactor surfaces. Helicon plasma source uses helicon waves excited in the plasma to couple RF power and uses a smaller magnetic field than the ECR source [Boswell 1970]. When the plasma is excited in this manner, the mean free path for electron collisions can become much larger than reactor dimensions, and the operating pressure can subsequently be lowered.

High-density sources render many processing advantages such as better dimensional control, higher etching rates, and selectivity. They enable operation at lower pressures making the sheath less collisional. In high-density sources, the wafer is biased by an independent RF source, thus making the ion energy and ion flux independent of each other. Since the typical ion energies are of the order of fractions of eV, ion acceleration in the negative sheath to hundreds of eV gives high directionality to the ions providing etch anisotropy [Lieberman 1993].

Deposition technology

IC fabrication requires deposition of both dielectrics and metals. The common dielectrics are oxides, nitrides and oxynitrides of Silicon, both doped and undoped. Oxide and nitride films have charge-storage property while oxynitride can render antireflection properties for the lithographic light [Bencher 197] and also function as a barrier film for gate conductors.

Time delay in response in microelectronic devices is due to the product of resistance and capacitance (RC) of the system. Lower dielectric constant material leads to lower capacitance, decreasing the interconnection delay and power dissipation [Murarka 1996]. The dielectric constant of silicon oxide can be reduced from 4.1-4.2 to 3.0-3.7 by doping the oxide with electronegative Fluorine [Laxman 1995]. Amorphous Carbon and fluorinated Carbon films have low dielectric constants (2.3-2.7) and thermal stability up to 400°C [Grill 1999].

The plasma CVD process is done in the millitorr pressure range. High electron density (10^{10} -10^{12} cm^3) and a high fractional ionisation rate (10^{-4} to 10^{-1}) are typical [Nguyen 1986]. Wafer is heated with Argon plasma to temperatures in the 300-400°C range, after which reactant gases such as silane, silicon tetrafluoride, organosilicon gases such as tetraorthosilicate (TEOS) are introduced. The RF power for deposition is then ramped up gradually to minimise damage to devices [Nakayama 1997]. Special consideration goes into the design of the vacuum system, which must have a high throughput and must withstand the harsh environment due to the presence of highly reactive gases [Baliga 1997].

Magnetron based sputter deposition is the key processes to deposit metallic layers for semiconductor devices. Sputtering produces an isotropic flux of metal atoms. At the low operating pressures, the deposition is a line of sight process. To enhance directionality, which improves deposition energy and the quality of the film, two techniques known as long-throw deposition and collimated sputter deposition have evolved. Narrowing the acceptance angle of the sputtered atoms results in a more normal incidence.

In a long-throw deposition system, the cathode-to-sample distance is increased, keeping the operating pressure low to reduce gas scattering. The result is that the isotropically expanding plume will intercept the target in a small cross-section, effectively giving directionality to the deposition, at the expense of losing a good fraction of the plume, typically 70 per cent. The second method to produce directivity is by collimating the neutral stream without increasing the source-substrate separation. This has the advantage that low pressures are no longer needed. Both processes can be seen to be inefficient in the use of sputtered atoms and result in low deposition rates.

The inability to steer neutral atoms in a controlled trajectory is at the root of the lack of directionality. However, if the neutrals are ionised, they can be directed by electric fields. In the late 1980s and early 1990s, systems were developed to increase the ionisation of metal atoms prior to deposition. When accelerated by an electric field, the ions will arrive at wafer surface normally. Since atoms are not filtered out, there is high utilisation of the sputtered atoms from the cathode.

A typical ionised PVD (I-PVD) system combines magnetron sputtering and in-flight ionisation of the sputtered atoms by an auxiliary plasma. The auxiliary plasma is produced by inductive discharge in the region between the cathode and the sample. As the sputtered atoms pass transits through the plasma, a fraction is ionised by electron bombardment. The efficiency of ionisation depends on the ionisation cross-section of the transiting atoms, the secondary plasma density and the transit time of the metal atoms through the plasma. At high pressure the sputtered atoms are slowed by gas collisions and spend more time in the discharge increasing the ionisation probability. The relative ionisation can be as high as 90 per cent at optimum conditions. The metal ions, on reaching the sheath covering the wafer electrode, are accelerated by the wafer potential. The efficiency of utilisation of the sputtered metal atoms can thus be quite high. High directivity of the ions enables deep features to be coated, for example, the bottom of contact holes. This technique has proven to be quite robust for semiconductor manufacturing applications.

The operation of magnetron plasma devices has been described in Chapter 3. However, the special features of magnetron systems used in semiconductor application should be highlighted. An ultraclean environment is essential to reduce the influence of ambient gas atoms on the structure of the deposited films. A deposition rate of 1 μm/min of Al corresponds to the formation of about fifty monolayers of Al per second. At 10^{-6} Torr pressure, background gas atoms arrive at a rate of 1 monolayer/s, and if completely incorporated into the film, it would constitute a 2 per cent impurity. At a base pressure of 10^{-9} Torr, the impurity flux can still be two parts in 10^5. When this is compared to the purity of a typical cathode (99.999 per cent), the effect of the contamination due to process can be of some concern [Rossnagel 1999].

The magnetron chambers used for large-scale semiconductor applications form part of a cluster tool. They use cryopumped stainless steel chambers with the base pressure generally in the low 10^{-8} Torr range for most cathodes, and in the 10^{-9} Torr range for Ti. The sorption pumping by the films deposited on chamber walls can contribute appreciably to the net pumping speed of the system. The working pressure during sputtering is in the millitorr range necessitating a gas flow of many tens of standard cubic centimetres per minute (sccm). The large gas flows demand frequent regeneration of the cryopumps. Wafers are introduced to the deposition chamber via a load lock and a degassing station, where water vapour adsorbed by the wafer is removed.

Commercial magnetron cathodes have diameters roughly 50 per cent larger than the wafer diameter. Structural considerations limit the cathode dimensions. The cathodes are water-cooled and are typically rated at powers of 20-30 kW limited primarily by the ability to cool the cathode by means of flowing water. The power supplies are switching supplies with sophisticated arc detection and suppression circuitry to reduce unipolar arc formation, which can result in microscopic particle deposition on the wafer substrate. The cathode materials used are generally Al (0.5 per cent Cu), Ti, Ta, and Cu. The purity is generally 99.99 per cent for the Ti and Ta cathodes, and 99.999 per cent or higher for the Al (Cu) and Cu cathodes [Rossnagel 1999].

Plasma Doping

Conventional beam-line implantation is used for controlled introduction of impurities into silicon to form junctions in semiconductor devices. As the devices shrink in size, deposition depth will correspondingly decrease demanding ultra-shallow junctions. Beam-line ion implantation technology fails at low energies since it is difficult to control the particle trajectories essential for beam quality. As the device geometry tends to even smaller dimensions, this problem is expected to aggravate.

Plasma ion implantation or plasma doping (PD) is being developed as a simpler, process with higher throughput. PD is compatible with cluster tooling and CMOS production environment. When a bias of several hundred volts is applied to the silicon wafer immersed in plasma containing the dopant species, positive ions are driven into and get implanted in the wafer. For accelerating voltages of 2-5 kV, implantation depths are of the order of 100 nanometers. Unlike beam-line implantation, the entire wafer is implanted simultaneously keeping the cost down. PD has high throughput since it has current densities of the order of 3mA/ cm^2 compared to typically 7μA/cm^2 available in beam lines.

Moreover, gas or solid sources can be used for PD. Gas source PD is usually performed in a B_2H_6 plasma diluted by He and sustained by an electron cyclotron (ECR) or radio frequency plasma source. The aim of dilution is to control the implantation rate. Gas sources tend to be toxic leading the drive for solid target PD.

The implanted junction depth is primarily determined by the energy of the ions and has been shown to vary linearly with this voltage over a range from 0.14 - 5 kV. However, there is no species-selectivity as in a line implanter. All ions present in the plasma are implanted. For example, with BF_3 gas, the predominant ions implanted are BF_2^+, B^+, and F^+.

The pulsed nature of PD produces a wide energy spectrum for the ions. This is due to the fact that the voltage pulse accelerates particles, which are situated in different regions of the sheath, which consequently fall through a space-dependent potential well. The finite rise and fall times of the pulse also contribute to the spread. While low-energy ions are not detrimental in shallow junction formation, both of these factors can affect the depth profile of the doped atoms [Jones 1996].

A limitation of the PD process is that only external parameters like pressure and voltage, plasma density, temperature etc. can be measured. These are inter-related in a very complex way. The plasma temperature determines the electron-molecule reaction rates and the plasma density. Plasma density determines plasma sheath expansion and thus energy and range of the ions when they impinge on the wafer surface. Plasma temperature in turn is controlled by gas pressure and total power coupled into the plasma. Complex theoretical models are used to relate the ion species, flux and energy to these directly measured parameters [Qin 1995]. The total current measured is a sum of ion, secondary electron and displacement currents [Jones 1997]. Relating the machine controllable parameters to the final dose and implant profiles require considerable theoretical work.

When processing wafers up to 300mm, the implantation spatial profile has to be uniform over this range. This calls for uniform plasma densities of this spatial dimension. Uniformity of 1.1 per cent has been obtained for selected energy ranges with 200 mm wafers. Generally, PD is capable of operating within a 5 per cent uniformity window for all energies.

Contamination is another crucial issue. The process roadmap demands metal contamination $<1 \times 10^9$ atoms/cm^2 in 2009. The decoupling of the contamination-rich ion source from the process chamber through the long drift tube in conventional ion implanters was a great advantage. Merger of the source, optics and process in PD does away with this advantage [Lenoble 1998]. The sources for PD system operate at much lower power densities compared to those for beam-line implanters and hence the wall can be made out of materials like Aluminium or Silicon which have a lower potential for contamination. Sputtering from the walls of the beam line is also absent. Cross-contamination is minimised by reserving the reactor for single species.

PD is considered to be benign from the point of view of plasma-based processing damage. The use of short pulses of implantation separated by relatively longer exposure to low-energy electrons from the plasma generates a self-limiting situation. Very short positive pulses have relatively low charge/unit area (about 1×10^{11} ions/cm^2 = 16 nC/cm^2) that will not produce significant electric fields in any dielectric ($E \sim 1.8$kV/m), so that one pulse will not introduce any significant leakage into the dielectrics. After this short pulse, a much longer time is allowed for the low-energy plasma electrons to neutralise the surface charge. Studies have shown that as long as the pulse frequency is kept below a threshold value, the plasma is able to fully neutralise the charge accumulated during the pulse.

The PD system for semiconductor processing consists basically of a vacuum system, plasma generation system and the implantation pulse generator. The vacuum system includes a turbo pump and a mechanical pump to achieve base pressures in the range of 1×10^{-8} torr and operating pressures in the range of 10 mtorr. A mass flow of about 2 sccm will require a pumping speed of about 150 litre/sec. The plasma generation system is one that has seen intensive development in many applications such as etch, CVD, and others. Most existing PD systems use either inductively coupled RF, or microwave ECR. Plasma confinement away from the wall to reduce impurity migration is crucial to the equipment design. This will also improve plasma uniformity. Wafer-handling and control systems, treatment systems for toxic gases and other subsystems are standard to other semiconductor processing systems.

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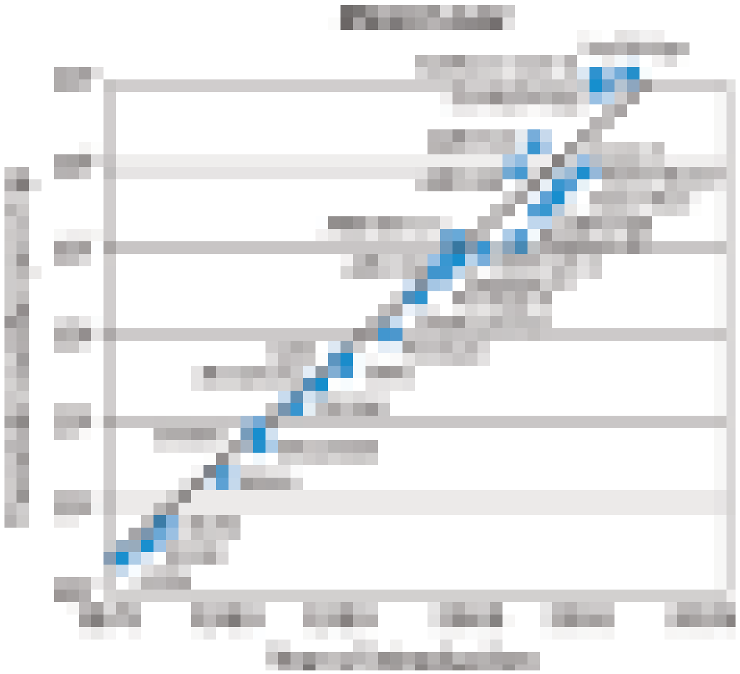

Fig. 13.1. Moore’s law as a measure of the increase in complexity of microelectronic devices with time

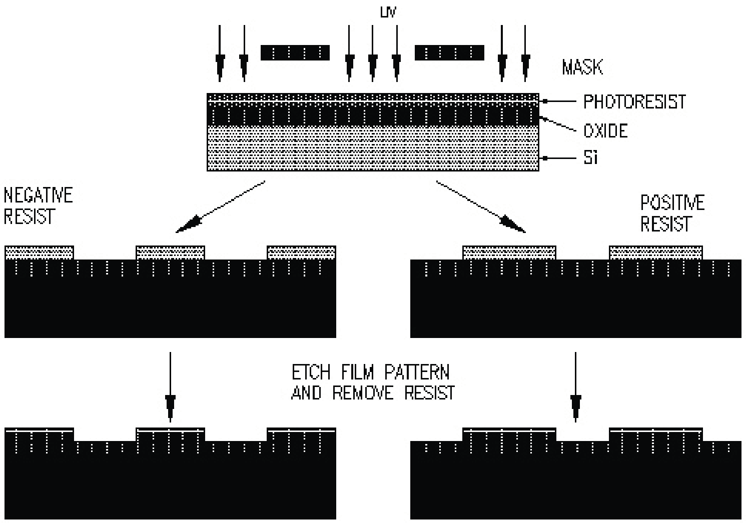

Fig. 13.2a. The basic steps in the fabrication of semiconductor devices

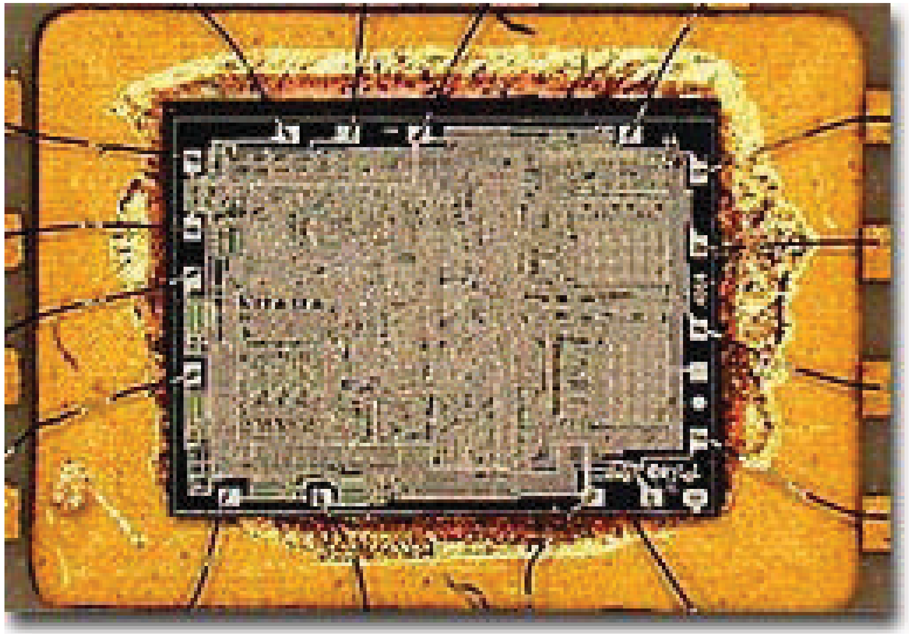

Fig. 13.2b. A microelectronic device

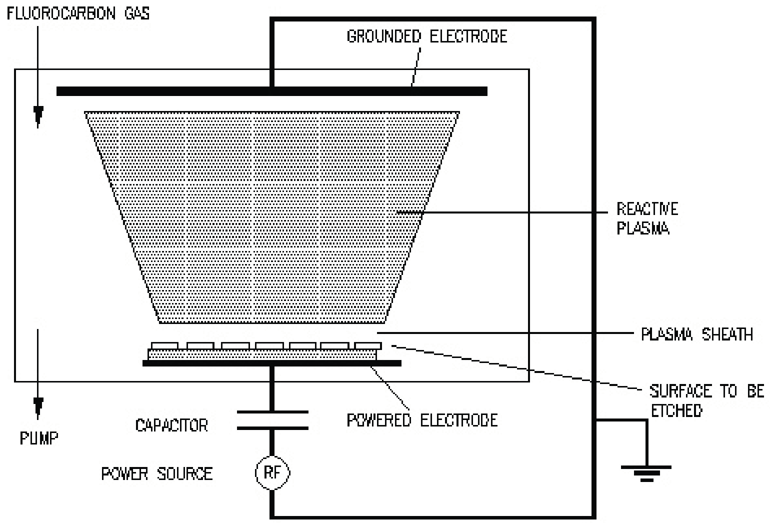

Fig. 13.3. Schematic diagram of a capacitive etching system

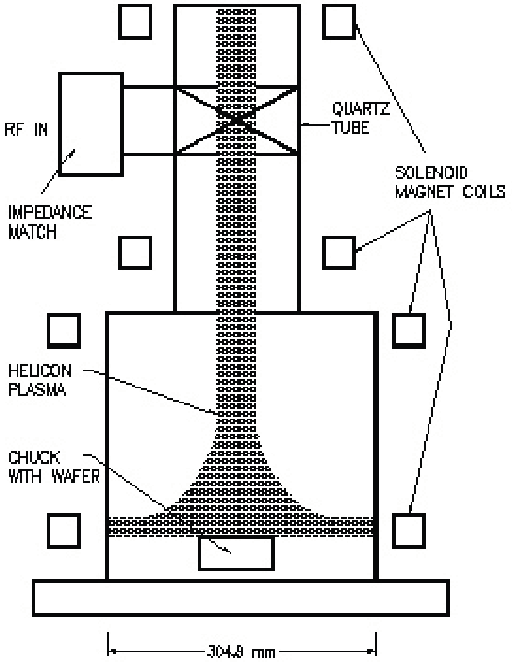

Fig. 13.4. Schematic diagram of high density Helicon plasma source. The RF energy is coupled to characteristic plasma waves

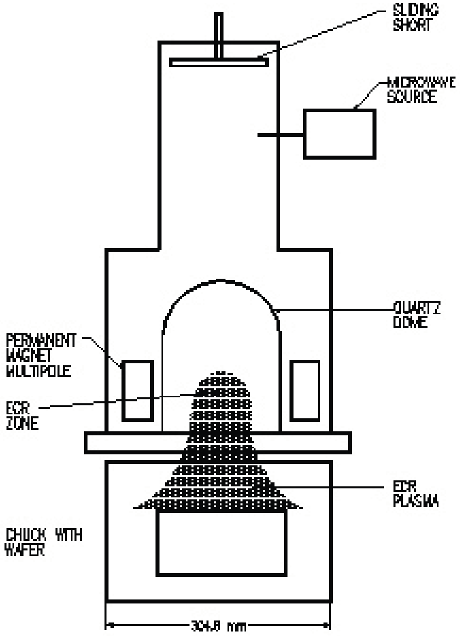

Fig. 13.5. Schematic diagram of high density ECR plasma source . The RF energy is coupled resonantly to electrons gyrating around the magnetic field lines

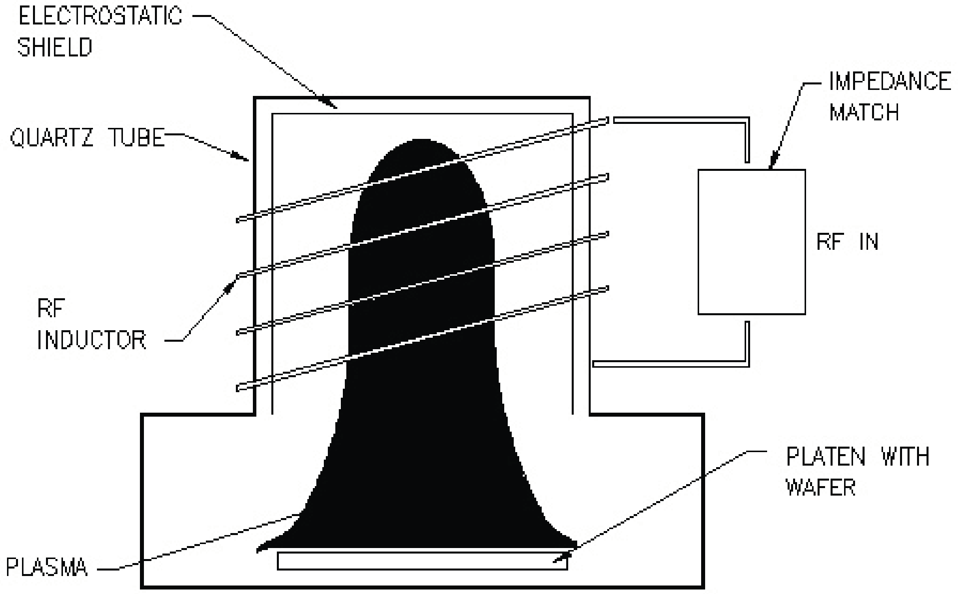

Fig. 13.6. Schematic diagram of an Inductive plasma source

14 Light Fantastic

Advanced Plasma Radiation Sources

Light emission in plasmas was one of the earliest plasma phenomena exploited for commercial applications. Excited atoms and molecules radiate light by a variety of phenomena. Starting with arc lamps and mercury vapour lamps, the technology has made immense progress over the years. Understanding the relevant plasma phenomena has aided in improving their efficiency and in tailoring the emitted light to mimic the natural light. This chapter examines the light emission phenomena in plasmas and the modern devices that commercially exploit them.

Natural and Artificial Light Sources

Aurora is the goddess of dawn in the Roman Pantheon. This is also the name given to the shimmering curtains of light shown in Fig. 14.1 appearing in the Arctic and Antarctic sky when energetic particles of the solar plasma -the solar wind-, deflected by the earth’s magnetosphere enters the polar atmosphere and ionises the air in the upper regions. The ionisation occurs about 70 miles above Earth's surface.

Lightning is another example of light generation by natural plasma. There is a slow, steady, flow of electricity from the surface of the earth and oceans to about 50 km up into the atmosphere. Tiny ice crystals moving in updrafts get charged by collisions with clumps of hail and transfer the charge to the cloud. The potential difference between the earth and the base of the clouds can reach hundreds of thousands of volts and can produce an electrical discharge to the ground. The spectacular show of light and sound is a consequence of the ionisation and heating of the air in its path. The lightning flash is composed of several strokes. The first, called the stepped leader, is made up of 1 ms, more than 1000 A spikes in electrical current separated by periods of lower current (50 ms, ~100 A) and originates from the cloud. This part of the lightning flash sets the jagged path that the next, more intense return strokes, which originate from the earth, will follow. The return strokes may have currents in excess of 30,000 A, each lasting for about 50 ms.

Inventors and designers have exploited the capacity of weakly ionised plasmas to emit light to create a dazzling array of luminaires [Elenbaas 1972]. Humphrey Davy, in 1802, demonstrated the creation of an electrical discharge in a rarefied gas between two electrodes connected to a battery. This was perhaps the first plasma light source. In 1814, Michael Faraday demonstrated a free burning carbon arc, in the Royal Academy of Science. In the 1850s, Einrich Geissler discovered that a discharge through a low-pressure gas gave off light of a spectrum characteristic of the gas, thereby founding both the neon sign industry and the science of spectroscopy. By proper choices of gases, Geissler was able to produce light of nearly all colours. The first commercial application of this principle was a display of multicoloured lights put on at Queen Victoria’s Diamond jubilee. Arons, in 1892, developed the mercury vapour arc, which evolved into the first commercial mercury lamp developed by Peter Hewitt in 1901. High pressure mercury lamps came in 1930's. Table 14.1 summarises the milestones in the development of discharge lamps [Gendre 2003].

Nonequilibrium Plasma as a Light Source

Plasmas emit electromagnetic radiation in a broad spectrum due to a variety of phenomena connected with atomic physics and charged particle dynamics. In plasma there is a large population of excited atoms and molecules with the electrons occupying high energy states. When the electrons relax to a lower energy state, they emit photons characteristic of the transition, giving rise to line radiation. Much of the visible light emitted by plasmas consists of spectrally selective light emitted by this process. Free electrons recombining with the ions emit spectrally dispersed light. Free electrons in the plasma also radiate electromagnetic waves, whenever their trajectory or velocity is changed. This can happen when they encounter an atomic nucleus. They emit bremsstrahlung radiation, a German word for breaking, implying the velocity change by the electric field of the nucleus. Free electrons gyrating around magnetic lines of force emit the cyclotron radiation and its harmonics. For low temperature plasmas, the radiation emitted by the electrons is in the microwave or infrared range.

Plasma light sources are electrical discharge devices maintained in a transparent glass envelope [Waymouth 1971]. The discharge is created in sub-atmospheric pressure gas mixtures or vapours of metals. The spectrum of the light places special demands on the optical characteristics of the wall material. The anode surface collects electrons and deposits heat related to the metal work function. Cathode has to provide electrons to maintain the discharge. Various schemes for easing the electron emission from the cathode involve lowering its work function and keeping it hot for thermionic emission. In most nonequilibrium plasma sources the light is emitted from either the negative glow near the cathode or from the positive column near the anode [Dakin 1991]. Low-pressure lamps have sharp line emission characteristic of the atoms in the lamp, and high-pressure lamps have broadened lines superimposed on a continuum.

The efficacy of a lamp is the ratio of visible radiation (luminous flux) to power input, expressed in lumens per watt. For a blackbody-like spectral power distribution in the visible, with zero radiant emission at any other wavelength, the luminous efficacy is about 200 lm/W at 100 per cent radiant power efficiency. The incandescent lamp of today produces approximately 15-25 lumens per watt with the balance of the electrical energy lost as heat. It is estimated that 40 lumens per watt is about as high as can be obtained by a Tungsten filament, just before it reaches the melting point (3370 degrees C.)

The second parameter quantifying a light source is the colour temperature, which is a representation of the colour emitted from a lamp, based on the colours given off from a black-body radiator (such as pure carbon) if heated to that temperature. Colour temperature is a measure of the 'whiteness' of a source and is expressed in degrees Kelvin. The specification of colour temperature technically applies only to incandescent lamps; Tungsten filament lamps used for general lighting applications have colour temperatures between 2600 and 3000 degrees Kelvin. The term 'apparent colour temperature' (or correlated colour temperature) is used to describe the degree of 'whiteness' for discharge lamps. The light from a cool white fluorescent lamp is similar to the colour of pure carbon heated to 4000 K.

The ability of a light source to accurately show colours is referred to as the colour rendering index (CRI). A light source, which is radiating in just blue, green, and red wavelength bands, will have acceptably good colour-rendering properties. Most coloured objects have sufficiently broad reflectance spectra that they reflect light in two or more of these bands, and the eye-brain system accepts a colour definition dependent on the ratio of these two intensities of reflected light. Light sources with such spectra can simultaneously have higher luminous efficiency than a broad-spectrum source while maintaining nearly equivalent colour-rendering properties.

Table 14.2 summarises the main characteristics of plasma based light sources.

Mercury Vapour Lamps

Electrical discharge in a mixture of argon and mercury vapour emits a characteristic light blue colour. The gas is the so-called Penning mixture. Argon has a metastable state as lowest excited state (11.56 eV) and the energy of this state is slightly greater than the ionisation energy of mercury, which is 10.39 eV. The de-excitation of the metastable state produces lots of photons, which can ionise mercury [Kenty 1950]. There are many mercury atoms with electrons in the 4.88 eV level and hence they emit lots of 253.7 nm photons. The inert gas also helps in starting the discharge, since in the cold state the vapour pressure of mercury is too low for discharge initiation [Henderson 1983].

Fluorescent lamps exploiting the process of fluorescence discovered by Sir George Stokes in 1852 brought a revolution in the lighting industry in 1938. Phosphor coating on the inside of the tube converts short-wave UV emission of low-pressure mercury into visible light. Magnesium tungstate is a common phosphor. Selection of phosphor can make blue, blue-green, slightly whiteish green, light yellow, bright pink, light purple, or white. The modern fluorescent lamp has an efficacy of between 65 and 100 lumens per watt.

Calcium and strontium activated halophosphate phosphors are the standard coating. This produces lamps with a moderately high efficacy, and moderately acceptable white light. Blending together several different halophosphate phosphors, with each covering different regions of the spectrum creates improved colour properties [Ostelten 1975]. The result is a lamp with a much higher colour rendering ability (Ra 93-98), but a lower efficacy (typically a reduction in light output of approximately 30 per cent, depending on the wattage).

The next development in the mercury lamp was the high pressure mercury vapour lamps introduced in 1934 which contain an internal arc tube made of quartz enclosed in an outer glass envelope [Ouweltjes 1951]. A small amount of metallic mercury is sealed in an argon gas fill inside the quartz tube [Fig.14.2a]. After the warm-up period, the arc emits both visible and UV light. High pressure mercury vapour lamps produce a blue-white light directly from the arc discharge. Phosphors similar to those used for fluorescent lamps can be used to give these a colour closer to natural light.

Sodium Lamps

Low pressure sodium lamps are the most efficient visible light sources in common use with luminous efficacy as high as 180 lumens per watt. A low pressure sodium lamp consists of a tube made of special sodium-resistant glass containing sodium and a neon-argon gas mixture. The electrodes are coiled tungsten wire doped with thermionically emissive material. Since the tube must reach a temperature around 300 degrees Celsius, the tube is bent into a tight U-shape and enclosed in an evacuated outer bulb in order to conserve heat. The inner surface of the outer bulb is coated with tin oxide or indium oxide that reflects infrared but passes visible light thereby reducing heat loss [Henderson 1983]. During the starting process, a low pressure discharge is established in the gases. This produces very little light but heats the metal contained inside the arc tube and gradually vaporises it. As this happens, the pressure increases and light production by the discharge through the ionisation of the high pressure metal vapour begins. A noticeable transition occurs when the light output increases dramatically over a period of a minute or more. The entire warm-up process typically takes 3 to 5 minutes.

More argon-rich mixtures are favoured today since hot glass has a propensity to absorb Argon from a low pressure electric discharge. Ideally the mixture should be only a few tenths of percent Argon in order to ionise most easily and do so much more easily than pure Neon or pure Argon. A significant surplus of Sodium is contained in the glass arc tube since the glass may absorb or react with some of the Sodium. The temperature of the coolest parts of the arc tube controls the sodium vapour pressure. When the arc tube reaches a proper temperature, further heating is reduced by the lamp's efficiency at producing light instead of heat.

The light of low pressure sodium consists almost entirely of the orange-yellow 589.0 and 589.6 nm Sodium lines. This monochromatic light causes a dramatic lack of colour rendition. Another disadvantage of low pressure Sodium light is that many objects will look darker than they would with an equal amount of light from other sources.

High pressure Sodium vapour lamps contain an internal arc tube made of a translucent ceramic material (a form of aluminium oxide known as "polycrystalline alumina"). Like other HID lamps, the arc tube is enclosed in an outer glass envelope. A small amount of metallic Sodium in addition to Mercury is sealed in a Xenon gas fill inside the ceramic arc tube. High pressure Sodium vapour lamps produce an orange-white light and have a luminous efficiency much higher than Mercury or metal halide lamps. High pressure Sodium lamps are roughly twice as efficient as fluorescent lamps. Unlike fluorescent lamps, HID lamps will give full light output over a wide range of temperatures. This often makes HID lamps more suitable than fluorescent lamps for outdoor use.

Metal Halide Lamp

Metal halide lamps are similar in construction to Mercury vapour lamps. However, in addition to the Mercury and Argon, various metal halides are included in the gas fill [Reiling 1961]. These vapours emit light to fill in the gap in the Mercury spectrum [Van Erk 2000]. Line radiators like Sodium and Thallium, multi-line radiators like rare Earth metals and Scandium, wide band molecular radiators like tin and rare Earth halides are used. Halides are used since pure metals have very low vapour pressure. The most popular combination is sodium iodide and scandium iodide. A few versions of this lamp have lithium iodide as well. The use of these compounds increases the luminous efficiency and results in a more pleasing colour balance than the raw arc of the Mercury vapour lamp. Thus, no phosphor is needed to produce a colour approaching that of a cool white fluorescent lamp with more green and yellow than a Mercury vapour lamp. Metal halide arc does not emit much UV and are 50 to 75 per cent more efficient than fluorescent lamps. About 50 per cent of the energy emitted by a metal-halide lamp is in the form of light, whereas the corresponding value for an incandescent lamp is about 10 per cent.

The colour of these lamps depends on the metal halides (usually iodides) and how much halide vaporises. Lower colour temperatures in the 3000 to 3500 Kelvin range indicate orange-yellowish shades of white, and the vapour in these lamps is rich in Sodium but also has smaller traces of Scandium and sometimes Thallium. Most metal halide lamps contain Sodium and Scandium halides and have a colour temperature near 4100 Kelvin (basically plain white) [Fig. 14.2b]. Some have less Sodium and more Scandium, and sometimes also other more blue-glowing metals like Indium, and therefore have a bluer colour.

The rare Earth halides react with the wall materials such as quartz and polycrystalline alumina. The Silicon and Aluminium released by this process can lead to corrosive damage and blurring of the wall as well as crystallisation and growth of porous deposits. This, in addition to the electrode erosion, is one form of mechanisms leading to reduction of lamp life.

Hollow Cathode Lamps

Hollow cathode lamps are a type of discharge lamp that produces narrow emission from atomic species [Jones1960]. They get their name from the cup-shaped cathode, which is made from the element of interest. The currents and pressure are such that the negative glow forms inside the cup drawing current from its internal surface area. The cathode forms a cylindrical potential barrier around the negative glow. Energetic electrons from the cathode surface make multiple passes through the negative glow and increase the plasma density. The proximity of the cathode maximises the cathode sputtering. Collisions with gas atoms or electrons excite the metal atoms to higher energy levels, which decay to lower levels by emitting light.

Hollow cathode lamps have become the most common light source for atomic absorption (AA) spectroscopy. They are also sometimes used as an excitation source for atomic-fluorescence spectroscopy (AFS).

Electrodeless Lamps

The Achilles' heel of the new genre of high efficiency discharge lamps such as metal halide lamps and high pressure sodium lamps is the electrode which eventually bum out. The electrodes also drastically limit the types of substances that can be used to generate light since many substances will chemically attack them.

Many complex processes happen at the electrodes exposed to the discharge plasma and continually subjected to bombardment of electrons and ions. Heating of the electrode makes it highly active chemically, and gases or impurities within the tube may react with it. Heavy ions sputter atoms off the electrode, which coats the inside of the glass tubes. Since the blackening caused by the metal deposit is confined to the ends of the tubes near the electrodes, this may be harmless. Eventually, of course, the process consumes the entire electrode.

The sputtered metal from the electrode sorbs the atoms of the fill gas in the tube reducing the pressure in the tube leading to what is called "hardening" of the tube. The reduced gas pressure makes the ion motion less collisional, thereby increasing the energy of the ions which, in turn, increases both sputtering and electrode heating.

Lamp manufacturers employ many techniques to make the electrodes last longer. Electrode area in increased to make them dissipate heat more efficiently. Sputtering reduces at lower temperatures. Metals, which have low sputtering yield, have been more or less standardised for each gas, pressure and operating current. Electrodes with ceramic collars at the forward end of the electrode are also used to protect the electrode. The ceramic collar acts as a buffer to prevent much of the sputtering. The electrodes can be coated with an electron-emissive coating, which will enable the tube to operate at a lower voltage thus reducing the electrical stress on the tube as well as damage due to sputtering.

Lighting industry has responded to these problems by dispensing with the electrodes [Forster 2001]. Electrodeless lamps are like transformers, where a time varying magnetic field in the primary winding induces time varying currents in the secondary. A high frequency current (2.6 MHz) is made to flow through a coil, which induces an electric field inside the lamp and ionises the gas. In 1994, GE Lighting introduced an electrodeless induction lamp, called the Genura lamp. The Genura lamp gives an efficacy of 48 lumens/watt and has a life of 10,000 hours. This process generates UV radiation, which excites phosphor on the inside of the tube, which emits visible light. The Philips QL lamp is another example, which uses magnetic cores excited by 2.65 MHz RF power to induce currents inside the lamp.

Lower frequencies are considered advantageous because of reduced electromagnetic noise. Osram Sylvania's Icetron system is an electrodeless fluorescent lamp excited by a lower frequency (250 kHz) alternating current. Ferromagnetic cores induce magnetic fields around the glass tube and currents are induced to flow in closed channels [Maiman 2000]. These lamps have an efficacy of 80 lumens/watt, a high colour rendering ability and an extremely long life of 60,000 hours. It works on a similar principle to that of the Genura lamp.

Conventional mercury lamps and most other high-intensity discharge sources are built around atomic emission and produce an artificial-looking light with many missing colours. The Sulphur lamp, developed by a US company, Fusion Lighting has a spherical quartz envelope filled with a few milligrams of Sulphur and an inert noble gas, such as Argon, which is ionised using microwaves to produce a high-quality white light. The Argon heats the Sulphur into a gaseous state, forming diatomic Sulphur molecules, or dimers. The dimers emit a broad continuum of energy as they drop back to lower energy states. Molecular Sulphur emits almost entirely over the visible portion of the electromagnetic spectrum, producing a uniform visible spectrum similar to sunlight but with very little undesirable infrared or ultraviolet radiation. Almost 75 per cent of the energy emitted from the bulb is emitted as light in a full-colour continuous spectrum. Lamps have a correlated colour temperature in the range of 4000-9000^{o} K.

The lamp is excited by microwave fields. The gas breakdown manifests itself as an avalanche-like increase in the electron density due to the collisional ionisation by electrons, which have been accelerated to high energies by the microwave electric field [Gurevich 1997]. Initial prototypes of the lamp are rated to produce 940,000 lumens for an electrical input of 5.9kW, which makes them far brighter than any other types of light source. The small size of the bulb makes it easier to design optically efficient reflectors, and the stable plasma makes it easier to predict the outcome of a given design. In the Forrestal Building in Washington, D.C., and the Space Hall of the Smithsonian's National Air and Space Museum a hollow pipe distributes focused light from the Sulphur lamp evenly over large areas. Fusion Lighting is developing a lower power version under the project name Solar 1000. Russian version of a similar device goes under the trade name Lightdrive. Philips Cluster lamp uses microwaves with a fill of mainly Tungsten and Argon.

Applying their expertise in electrodeless discharge lamps, scientist from Lawrence Berkeley Laboratories developed lower-power lamps using radio frequencies instead of microwaves. In 1993, they demonstrated a RF-driven Sulphur lamp that produced up to 15,000 lumens with a RF input of only 100 watts - a luminous efficacy of approximately 150 lumens per RF watt. While the lamps still needed to be rotated, lower-power operation allowed the air cooling to be eliminated.

Plasma Globes

In contrast to its use in lighting and advertisement, several fine artists over the last 30 years have used electrical discharges as an art medium. The most popular of these plasma sculptures can trace its lineage back to Nikola Tesla, the inventor of Tesla resonant transformer or Tesla coil, among other things. This is the plasma globe, which is also known by other names such as plasma sphere, lightning globe, nebula ball etc. The enigmatic and constantly changing streamers of light is quite enchanting. A successful commercial version was called “eye of the storm”.

The device is an evacuated glass sphere with a central electrode and filled with gas at pressure in the range of 1-100 torr [Guilbert 1999]. The central electrode is usually made of iron wool to create strong localized non-uniformity in the electric field. It is energised with a high voltage-high frequency power supply. Typical voltages are around a few thousand volts for most commercial plasma globes. Typical frequencies are from a few to a few tens of kilohertz. The high voltage breaks down the gas into luminous streamers, and the high frequency gets the current through the glass of the globe and into the surrounding air by capacitive coupling.

The pressure needs to be high for streamers to form. The plasma filaments get hot and rise by buoyancy making the streamers move rather randomly up the side of the globe. Also, this hotter region has much higher conductivity and therefore the streamers remain intact until an instability breaks them. Charge builds up in areas without trails until they ionise. Then the charge carriers in a cloud region collapse into an ion trail, which is a good conductor, which allows current to flow to circuit ground, draining the charge. Once the region is discharged, the trail may disappear or migrate in some direction towards another area, which is charged. The trail will continue to exist as long as sufficient current can flow.

Mercury-free Fluorescent Lamp

The mercury vapour in florescent lamps is so efficient that it transforms nearly 75 per cent of the electrical energy into ultraviolet radiation. However, Mercury is considered to be a hazardous material and there are growing environmental regulations concerning the disposal of Mercury filled lamps. Fluorescent lamps are coming under increased scrutiny because of their Mercury content.

Alternate methods of generating UV radiation based on Dielectric Barrier Discharge or DBD have been developed by Siemens. Originally developed in 1857 by Werner Von Siemens as a method for producing ozone, DBD has been limited to specialised ultraviolet radiation sources [Eliasson 1988]. The biggest advantage of DBD is that it allows intense UV radiation to be generated even using noble gases such as Xenon rather than Mercury. Its disadvantage was that it was characterised by a deplorable 15 per cent efficiency. This is caused by the randomness of the discharge associated with a high level of electron density and low efficiency. To produce well-defined starting conditions for the electrons, short excitation pulses followed by idle times that are exactly long enough to allow the ionised gas to return to the state it was in prior to excitation are used to drive the discharge.

As the flat lamp, which was eventually christened Planon, took shape, it became apparent that it would have an impressive list of benefits. For one thing, thanks to reduced wear on the electrodes, it lasts far longer than just about any other florescent lamp with conventional electrodes on the market - up to 50,000 hours. Since it does not contain Mercury, which takes up to several minutes to warm up, Planon switches to full brightness instantly without the slightest flicker, providing an even, white glow from edge to edge. It is also virtually impervious to temperatures, functioning with undiminished efficiency in a range from -30 °C to +85 °C. And again, because of the absence of Mercury, the lamp presents no problems in terms of disposal. Because of its regular geometry, the product is also easy to manufacture, package, transport and store, allowing for a high level of process automation. Finally, being only one centimetre in thickness, Planon can be manufactured in almost any diagonal dimension. Planon's one drawback is that it is still not quite as efficient as mercury-based florescent lamps.

Another contender for replacing mercury is discharge lamps with a mixture of Molybdenum oxide (MoO_3) and Argon [Giuliani 2003]. The vapour pressure of MoO_3 rises from 1 torr at 1000°K to 20 torr at 1085°K. Once ionisation starts, kinetic processes dissociate MoO_3 and the Mo radiates in near UV and visible spectrum. The strongest UV emission is at 320 and 390 nm, and to convert them into visible light, new phosphors are required. The efficacy for experimental devices is 40 lumens/watt.

Economic and Environmental Dimensions

Worldwide turnover of the lighting industry is estimated to be more than 15 billion dollars. Light sources, in addition to lighting, find application in several important industrial domains, for example, reprography, surface treatment, water and air purification, polymer curing, and process monitoring and control. If these additional applications are taken into account, the total word-wide turnover of light source related technology is 2-3 times higher than the above figure.

Currently, more than 7.5 billion lamps operate worldwide consuming more than 2,000 billion kWh per year (10-15 per cent of the global energy production). If, for an industrialised country, this amount is substantial (e.g. about 11 per cent for France, 20 per cent for US) it becomes very important for poorer nations for which lighting is one of the major applications of electricity (i.e. 37 per cent for Tunisia and up to 86 per cent for Tanzania). It is estimated that the need for light sources will increases by a factor of 3 in the future. More efficient light sources would limit the rate-of-increase of electric power consumption; reduce the economic and social costs of constructing new generating capacity; reduce the emissions of greenhouse gases and other pollutants. In fact, an improvement of 25 per cent in the lamp efficacy corresponds to 250 billion kWh per year energy savings as well as 150 million tons less greenhouse gas in the atmosphere.

A large number of studies have been completed and published on the potential of energy savings through energy conservation measures. For example, the commercial building sector, with more than 40 billion square meters of space in place, represent 30 to 35 per cent of total electrical demand. It utilises 5 to 10 per cent for air-conditioning necessary, in major part, for cooling air and building fabric heated directly or indirectly by current light generation technologies. Various estimates have indicated a potential for energy savings of 25 to 50 per cent in the commercial sector by utilising newly available lighting technology. From the viewpoint of lighting design, the main focus of attention has been to increase the average efficiency from the range of 40 to 50 lumens per watt achievable using older fluorescent technology towards the figure of 100 lumens per watt made available using the more recent fluorescent lighting systems.

Fluorescent lamps dominate the area lighting market. It is estimated that 1.2 billion lamps are manufactured each year world-wide with Japan being responsible for 20 per cent of this total. These light sources, as do several other commercially important types, contain a small amount of Mercury. As a consequence, at the end of the lamp lifetime a considerable amount of toxic waste is generated. For example, 80 tons of wastes containing Mercury are collected each year in France. If highly toxic Mercury were eventually to be prohibited as a lamp material on environmental grounds, there would be a great challenge to develop of new generations of light sources with greater efficacy than is available at the present time.

Efficiency of conversion of electric energy into light by commercial light sources, which has been increasing steadily, appears to have reached a plateau of about 33 per cent of the theoretical maximum [Fig. 14.3]. No truly revolutionary new light sources have been introduced since the mid-1960s, marked by the debut of metal-halide and high pressure Sodium arc discharge lamps. Light source developments since then have been primarily evolutionary, with incremental improvements in efficiency. Overall system gains in lighting efficiency have in the last decade primarily resulted from the substitution of more efficient sources for less efficient ones (viz. compact fluorescent replacing incandescent). To achieve the continued load-saving challenges that will be required in the future, much greater efficiency improvements, by about a factor of two, will be required.

All of the major lamp manufacturers in the US and Europe have for many years maintained significant applied research and advanced development groups unburdened by day-to-day problem-solving responsibilities but immersed in a highly-focused corporate climate. A fundamental reason for the present plateau in efficiency of light sources appears to be a drying up of the new scientific base that has supported the technology since its inception: atomic physics and spectroscopy, and electron and plasma science, electronics and electrical engineering. Thus, the development of revolutionary new light sources can only be based on new scientific phenomena not previously considered for light source applications.

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Year	Inventor	Product
1802	Humphrey Davy	Carbon arc
1856	Henrich Geissler	Glow discharge lamp
1859	Gustav Kirchof	Spectral lines
1901	Peter Hewitt	Low pressure mercury lamp
1920	Osram	Fluorescent lamp
1931	Philips, Osram	Low pressure sodium lamp
1932	GEC, England	High pressure mercury lamp
1961	Gilbert Reiling	Metal halide lamp
1965	General Electric	High pressure sodium lamp

Table I: A Brief History of Plasma Based Lamps

LAMP	EFFICACY	CCT K	CRI	AVG. HOURS
Mercury Lamp	55 - 60	3300-5700	15-55	12-24,000
Fluorescent Lamp	65 -100	3000-6500	52-92	10-20,000
HPS Lamp	80 -140	2000-3200	22-75	10-15,000
LPS Lamp	120 -200	1600	0	16,000
Metal Halide Lamp	85 -120	3000-5200	65-80	6-20,000
Compact Source Iodine	70 - 80	4000	85	500
XENON		6000	95	800-2,000

Table II: Characteristics of Discharge Lamps

Fig. 14.1. The Aurora Borealis: light emitted by the ionisation of air by solar wind particles

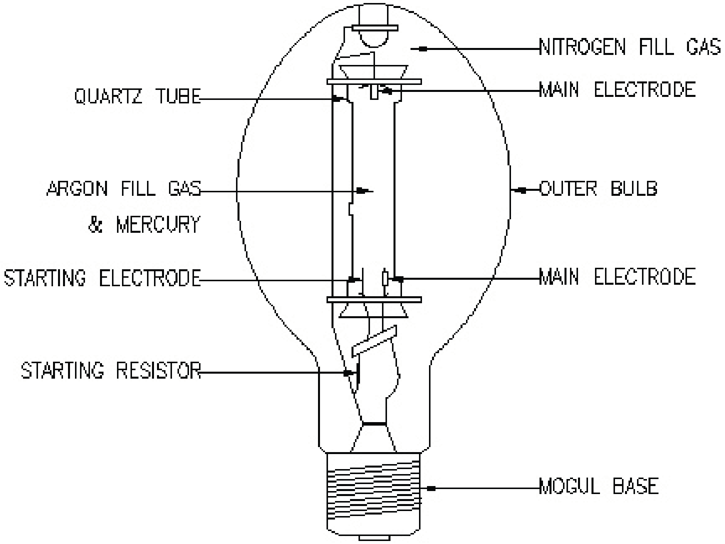

Fig. 14.2a. Schematic diagram of a high pressure mercury vapour lamps

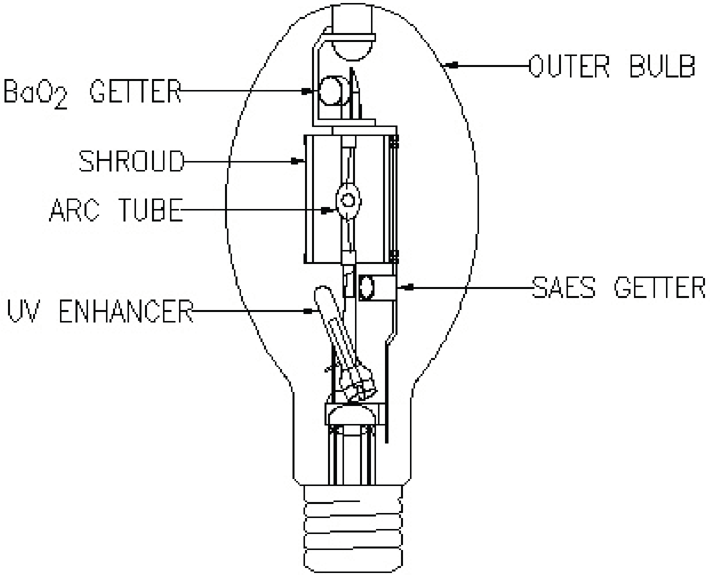

Fig. 14.2b. Schematic diagram of a Metal halide lamp

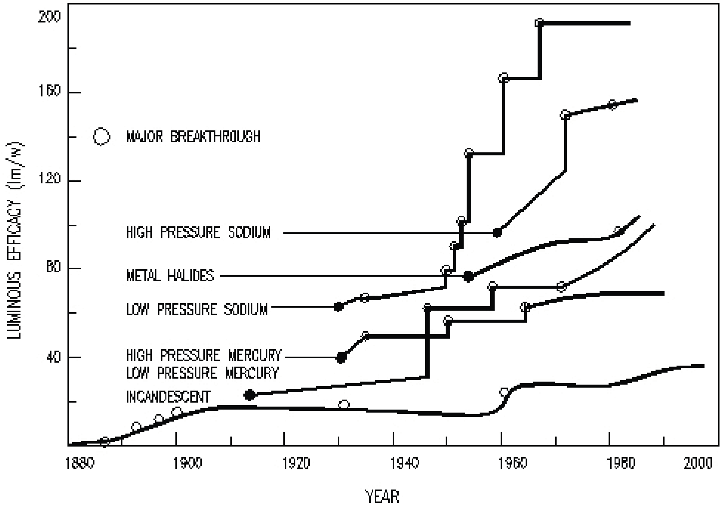

Fig. 14.3. The steadily increasing efficiency of lighting sources over the years

15. And Now on the Silver Screen

Plasma Techniques for Visual Displays

Giant screens with bright images are displacing the conventional television set in the living room. High definition displays using plasma panels is a major contender in the growing entertainment market. Plasma display panels use a programmable matrix of tiny plasma sources to display images. This chapter describes the basic properties of plasma display panels and their future.

Flat Panel Display Technologies

Many consider television as one of the most successful commercial products. Its bright images dazzle millions of viewers across the world. Movies from Hollywood and Bollywood are brought to comfortable viewing at home. The pronouncements of pundits on current events form public opinion and MTV sets the standards on pop culture.

Television's picture is formed in the cathode ray tube - CRT for short. Electrons emitted from a hot filament are accelerated and focused into a beam and shot at a screen coated with phosphors [Fig. 15.1]. The beam spot interacting with the phosphor emits light. Applying electric fields can make the beam spot move up, down or laterally. By modulating the beam intensity, the light intensity is varied. Invented in 1897, the cathode ray tube is still the most common display technique today. It features advantages such as high response speed suitable for high-frame rate, high-resolution video, wide viewing angle, saturated colours, high peak luminance, and high contrast.

If cheap, mass manufactured CRT's drove television's commercial success, the paramount rule of consumerism -bigger the better- sees it as its Achilles' heel. The problem with CRT is that it has reached a limit in size. CRT is a glass shell evacuated to low pressure to keep the electron beam intact from scattering with gas atoms. As the size increases the atmospheric pressure exerts increasing force on the glass envelope. Hence it is not viable to make tubes beyond a critical size. 40 inches diagonal is apparently the limit. Larger tubes would be too heavy and unwieldy because of the box shape. CRT has been regarded as hazardous for long-term use due to X-rays generated by electrons hitting the screen. The limited end-of-life disposal options for leaded glass, mixed plastics and other components of the display make it an environmentalist's nightmare.

The size limit will start to really hurt the TV industry with large-scale broadcast deployment of the high definition TV (HDTV) that appeared in the market in the 1980's. HDTV is capable of producing images having essentially the same details as a 35 mm film. The high resolution HDTV technology will have a significant effect on viewers only if it is projected on large screens, typically above 40 inches [Sobel 1998].

The bulky CRT is being squeezed out of the market by slim versions of display devices [Tannas 1985]. Field emission display (FED) is one of the options. Instead of using a single bulky vacuum tube, FED uses tiny micro tubes for each pixel. The single beam of the CRT is replaced by thousands of beamlets, each driving a pixel. A thin version of the CRT developed by US based Candescent Technologies uses a 3.5 mm thick flat panel formed out of two sheets of glass plates separated by a 1 mm gap. Very thin ribs made of a ceramic material support the plates from collapsing under vacuum. The ribs are thin enough to be hidden between pixels without affecting viewing. The faceplate is coated with conventional colour phosphors. The electron beam is generated from cathodes made from nanometer sized sharp points of materials such as Molybdenum and Silicon, from which electrons can be pulled off easily by an intense electric field. Each tiny electron beam excites the colour phosphors at the front of the cell. FED generates light from the front of the pixel, so the viewing angle is excellent; 160 degrees both vertically and horizontally. The display will show all green information first with red followed by blue. FEDs also have redundancy built into their design, most designs using thousands of electron emitters for each pixel. FEDs suffer no loss of brightness even if 20 per cent of the emitters fail. While a CRT has just one vacuum tube, a SVGA FED needs 480,000 of them. Manufacturing appears to be a bottleneck, though six-inch colour FED panels are already in the market.

Display based on liquid crystal technology is another viable competitor to CRT. Light passing through liquid crystals follows the alignment of the molecules that make them up. Applying an electric field change their molecular alignment, and consequently the way light passes through them. LCD works by letting varying amounts of a fixed-intensity white backlight through an active filter, which separates red, green and blue colours. Since its advent in 1971 as a display medium, liquid crystal displays have moved into a variety of fields, including miniature televisions, digital still and video cameras and monitors and laptop computers. Today many believe LCD to be the most likely technology to replace the CRT monitor.

Most liquid crystals are organic compounds consisting of long rod-like molecules, which, in their natural state, arrange their long axes in a loosely ordered fashion. It is possible to precisely control the alignment of these molecules by depositing the liquid crystal along a finely grooved surface. The alignment of the molecules follows the grooves. If liquid crystals are sandwiched between two surfaces with fine grooves on each surface orthogonal to each other, light will follow the alignment of the molecules, and therefore is also twisted through 90 degrees as it passes through the liquid crystals. When a voltage is applied to the liquid crystal, the molecules rearrange themselves vertically, allowing light to pass through untwisted.

Natural light waves are randomly polarized. A polarising filter is made of microscopic parallel lines, which blocks all light waves except those polarized parallel to the lines. A second polarising filter with lines arranged perpendicular to the first would therefore totally block this polarised light. Light would only pass through the second polariser if its lines were exactly parallel to the first, or if the light itself had been twisted to match the second polariser. A typical twisted nematic (TN) liquid crystal display consists of two polarising filters with their lines arranged perpendicular to each other, which, as described above, would block all light trying to pass through. But in between these polarisers are the twisted liquid crystals. Therefore, light is polarised by the first filter, twisted through 90 degrees by the liquid crystals, finally allowing it to completely pass through the second polarising filter. However, when an electrical voltage is applied across the liquid crystal, the molecules realign vertically, allowing the light to pass through untwisted but to be blocked by the second polariser [Fig. 15.2].

In an active matrix liquid crystal display (AMLCD), an extra matrix of thin film transistors (TFT) are connected to the LCD panel - one transistor for each colour (RGB) of each pixel. These transistors drive the pixels, eliminating the problems of slow response speed that afflict conventional LCDs. The result is screen response times of the order of 25ms, contrast ratios in the region of 200:1 to 400:1 and brightness values between 200 and 250 cd/m^2 (candela per square metre). The liquid crystal elements of each pixel are arranged so that in their normal state (with no voltage applied) the light coming through the passive filter is 'incorrectly' polarized and thus blocked. But when a voltage is applied across the liquid crystal elements they twist by up to ninety degrees in proportion to the voltage, changing their polarisation and letting more light through. The transistors control the degree of twist and hence the intensity of the red, green and blue elements of each pixel forming the image on the display. The thin-film transistors are formed from polysilicon thin films deposited on a glass substrate.

An innovation in display technology is the Digital Light Processor developed by Texas Instruments. A matrix of millions of hinged, tiltable mirrors are formed by silicon micromachining. Each mirror can be activated by external command, changing its orientation and reflecting light to form an element of a picture. Complicated optics is needed to convert a picture into a projectable display. To produce colour, three separate devices can be used, each illuminated with a primary colour, or alternatively, one device can be placed behind a rotating colour wheel with the chip displaying red, green and blue components sequentially. While the mirror chip is currently only available in projectors, it’s likely that they will appear in a back-projecting desktop display eventually.

All of the displays discussed so far are two-dimensional. Development of holographic autostereoscopic display (HAD) technology is expected to bring true 3D holographic screens to the consumer market by 2005. Holographic display will replace LCD's backlight with holographic optical element. This is divided into two sets of horizontal bands that correspond with each eye. The result is that the left eye sees one image and the right eye sees another, thereby achieving a 3D effect. Major application will be to computer games. Its principal limitation is that the image can distort if the viewer shifts position.

Plasma Display Panels

Plasma displays produce light by ionising a low-pressure inert gas [Slottow 1976]. By applying a voltage equal to the breakdown voltage of the gas to two electrodes in a minute gas-filled discharge space, the gas is ionised and converted into plasma. In this state electrons are removed from the atoms by the applied electric field. When the electrons recombine with the ions, they release light energy in the form of photons and the gas glows with a colour characteristic of the gas. After a while, the excited atoms return to their original state and energy is dissipated in the form of ultraviolet radiation.

The high non-linearity in the electrical characteristics of gas discharges is the key to their adaptation to display technology. Below a threshold voltage there is no plasma or emission of light. Above this, the light as well as current increase by many orders of magnitude. This allows a large number of discharge elements to be independently turned on or off without significant cross talk. This is to be contrasted with the liquid crystal display, which require another non-linear element such as the thin film transistor to be put in series [Weber 1985]. PDP picture elements also have the advantage that the emission of light is Lambertian, allowing a large viewing angle, typically 160°. The discharges have high impedance making the drive electronics simple. The inherently low capacitance (100 times smaller than liquid crystal displays) make them respond faster to voltage changes; an advantage where high-speed video is displayed.

An early form of plasma display was the Nixie [Jackson 1975] or numerical indicator tubes manufactured by the Burroughs Corporation. Ten cathodes each shaped like a number are serially excited to produce a glow discharge in a Neon-Argon mixture and the glowing cathode indicates the number displayed. Although nixie is now obsolete, it was, apart from CRT, the dominant electronic display technique around 1950 and its success led to the development of present flat panel display devices. The column and row matrix plasma displays of the present began development in the early 1950s and were the first commercially available panel displays.

The Nixie tube had an anode in a row intersecting many cathodes in a column with each intersection point being capable of creating a minuscule discharge. Extension of this idea leads to a row of anodes intersecting a column of cathodes, a matrix display, which is capable of creating a complex image. However, when energized by a dc voltage, each discharge, being a low impedance element between electrodes creates unwanted coupling between rows and columns. In principle using a series resistor with each electrode could eliminate this. However, a very elegant solution to this problem was to replace the dc excitation with ac and create capacitive impedance by interposing a thin glass plate between electrodes [Slottow 1976]. Industrial support to this concept soon led to the development of the 512 x 512 matrix plasma display [Hoehn 1971]. This formed the foundation of the present day plasma display devices.

Plasma display panels are conceptually simple. The external body is made of two sealed glass plates separated with a gap of 200 microns and filled with gas at sub atmospheric pressure, typically 500 torr. Thin parallel electrodes are deposited on the inner surface of the glass plates. The top plates have row electrodes; the bottom one has columns, perpendicular to each other. The intersection of each row and column electrode can produce an independent microscopic gas discharge if an appropriate voltage is applied. The plasma emits visible and ultraviolet light. In colour PDPs the ultraviolet light is used to excite phosphors, which can emit red, blue or green light.

The electrodes can be driven electrically with either DC or AC voltage. In AC discharges the electrodes are covered with a dielectric layer, typically an enamel. Two types of AC PDPs are possible. In the opposed electrode type the discharge strikes between electrodes on different plates. In the more prevalent coplanar type, the discharge strikes between electrodes on the same plate and is triggered by the electrodes in the opposite plate.

Figure 15.3 gives a schematic representation of a coplanar colour PDP. The electrodes on the front plate are called sustain electrodes and the discharge occurs between row and column electrodes on the back plate. The electrodes are transparent and are covered by an enamel and a thin (few hundred nanometers) layer of magnesium oxide. The dielectric layer has many functions. It protects the electrodes from the ion flux and subsequent damage and increases the secondary electron emission. The current and duration of the discharge are also limited - a basic characteristic of dielectric barrier discharges. The dielectric layer also produces a ‘memory’ effect. The charge stored in the dielectric during a discharge produces an electric field, which aids the discharge in the reversed polarity cycle. Hence the voltage required for subsequent operation remains lower than what was needed to initiate the discharge.

Magnesium oxide is the preferred coating over the dielectric. Uniform deposition of MgO film can be obtained over large areas by electron beam evaporation of MgO bulk material. The secondary emission properties of MgO remain unchanged even when its thickness reduces due to sputtering. The deposition has a lifetime of over 10,000 hours, which actually determines the life of the display. The rear glass plate has the address electrodes, which are used to switch the discharge on and off. In order to decrease the optical interaction between pixels, dielectric barriers called ribs are deposited between the address electrodes. The rear plate and the sidewalls of the ribs are coated with colour phosphors. The picture element, pixel, is formed by the intersection of a pair of sustain electrodes and one address electrode.

In operation, a square wave pulse of frequency 50-250 kHz is constantly applied to sustain electrodes. This voltage is just below the breakdown voltage. To turn a certain pixel on, an additional ‘write’ voltage pulse is applied to the address electrode and one of the sustain electrodes. The resulting discharge is quickly quenched due to the surface charge on the dielectric covering the electrodes. However, on the next cycle the sustain voltage changes polarity. The stored charge is drained and a new discharge takes place. In this way new transient discharges take occurs at each half cycle. Applying an erase pulse to the address and sustain electrodes turns off the pixel.

PDPs belong to the active or emissive class of displays. The device itself emits light and hence there is no need for external illumination. The emission is quasi-instantaneous, providing a response time of few nanoseconds for the device. The information being displayed is bright and easy to see, even in the presence of ambient light. The brightness is independent of the number of display elements used. Displays operating with inherent memory produce images that are flicker free since the image is not being continuously updated. In addition to picture quality, full colour displays are currently capable of producing up to the standard 16.7 million colours as in computer CRTs. This may increase as phosphor luminescence technology improves. The emissive nature of PDPs produces viewing angles up to 160^{o} compared to the 55^{o} viewing angle available with LCDs.

One of the major advantages of plasma displays is the large display size that is possible with a very small depth compared to a CRT in which the depth is roughly equal to the diagonal of the screen. Glass plates sandwiched closely together in a PDP create the small depth of display. The small depth makes plasma displays low in volume and weight even when compared to other types of flat panel displays that are comparable in size. The PDP is easily scaleable, making large screens possible. Also, a factor in enabling scale up to large screens is the fact that AC plasma displays don't need to be refreshed due to the panel’s inherent memory. The charging of the dielectric surface gives the pixel a memory, which enables rapid turn-on with any arbitrary delay. Therefore, the brightness is independent of the screen size. Because the surface of the PDP is completely flat, images being displayed are distortion free and clear across the panel. PDPs also have fixed picture elements making them aberration free.

Xe generates atomic resonance radiation at 147 nm and a molecular band centred on 173 nm [Yoon 2000]. However, the breakdown voltage of Xe is very high and to bring it down, it is mixed with 90 per cent Neon. Neon ions are also good in producing secondary electrons. The total ionisation coefficient of the Xenon-Neon mixture can be larger than the ionisation coefficient of pure Xenon and Neon [Boeuf 1997].

Luminance and contrast, the ability to interpret the display in the presence of ambient light, are related. Gray scale, the number of discrete shades to which a pixel can be set has been a problem in the performance of plasma displays. Output should be zero upto a well-defined threshold voltage and then must rise. The increase should not be too abrupt, since the gray scale, is to be achieved by controlling the amplitude of excitation. Furthermore, this curve must repeat precisely from pixel to pixel. This is done by turning on an element for varying lengths of time within a frame (duty factor modulation). This approach has also been applied to liquid crystal displays.

Another type of plasma display uses the plasma as a source of electrons rather than photons. The electrons are accelerated to excite cathodoluminescent phosphors, which emit light in different colours. This type of device has been demonstrated by Siemens in both monochrome and in colour and has a typical size of 12 in diagonal. Other companies working on similar concepts are Lucitron and Toshiba. The cathodes of Lucitron's 8 in diagonal flat screen device are hollow cathodes, a geometry that increases the effectiveness of cathode and reduces the required voltage.

To generate colour shades, the perceived intensity of each RGB colour must be controlled independently. This is done in a CRT by modulating the electron beam current, and therefore also the emitted light intensities. In PDPs this is accomplished by pulse code modulation (PCM). Dividing one field into eight sub-fields, each with pulse weighted according to the bits in an 8-bit word, makes it possible to adjust the widths of the addressing pulses in 256 steps. Since the eye is much slower than the modulation rate, it will integrate the intensity over time. Modulating the pulse widths will therefore translate into 256 different intensities of each colour. The number of colour combinations is therefore 256 x 256 x 256 = 16,777,216.

There are two fundamental methods of driving a PDP; refresh operation or memory operation. Refresh operation is implemented using the line sequential scanning method. To operate in this mode, the driver circuitry must provide a line sequential scanning circuit and data input circuitry for each row and column. A switching driver selects a pixel using a data and scanning signal applied to the corresponding row and column. This process is repeated at a specific frequency, completely rewriting the display each cycle. As displays become larger, however, the refresh frequency decreases leading to a visible display flicker. Techniques available to combat this problem include scanning two columns simultaneously or implementing a row scanning system.

On the other hand, memory operation overcomes the need for refresh cycles. To control a display via memory operation requires the ability to apply three signals to each cell. First, the sustain voltage must be maintained to keep the cell active. Second, a writing voltage must be provided for a period of time to turn the cell on. Finally, a blanking voltage needs to be provided to turn each cell off. As with refresh operation, each row and column must have this driver circuitry.

The major complication in the development of driver technology for plasma displays is the high voltages -150 to -250 volts that must be provided. Standard TTL and CMOS circuitry cannot handle voltages of this magnitude. Solution has come in the form of a hybrid IC package combining high voltage drive circuitry with a low voltage shift register. High voltage drive circuitry employing double-diffused metal-oxide semiconductor and CMOS shift registers bridges the gap between the low voltage technology of the processor and the high voltages required by the driver circuits.

In the drive towards thinner display panels, typically 3-4 inches thick, space is a premium. This poses problems for implementing the drive circuitry. Each row and column must have its own drive circuit. As display resolution is increased, more driver circuitry is required in the already cramped space. Recent successes in the implementation of chip-on-glass technology have provided an encouraging solution to the problem. This technology allows row and column driver ICs to be mounted directly on the glass, thus solving interconnection difficulties and reducing the weight of the display.

PDPs consume high power compared to other types of flat panel displays. For example, AC-PDPs have an operating voltage of 50-100V compared to between 2 and 5V for a liquid crystal display. DC-PDPs have an even higher operating voltage of 180-250V. This high voltage requirement is due to the high threshold voltage needed to excite the gas itself. Current consumption is also high, 1-10 mA/cm^2 for both AC-PDPs and DC-PDPs, compared to 1-10 μA/cm^2 for liquid crystal displays. Phosphor efficiency is very low; 1 lumen/W compared to common fluorescent phosphors, which achieve 80 lumens/W because the present phosphors are not optimised for the Xenon spectral emission. With optimisation of the phosphor efficiency the power efficiency can increase. The major life-limiting process in plasma displays are sputtering of the cathode material, cleanup of the gas and leakage, either of gas out of the panel or of air into the panel. Also, the discharge process causes sputtering of the cells, which inevitably reduces lifetime. With the protective dielectric layer of MgO, however, this problem has largely been solved.

Despite these problems, PDPs hold some promise because of their modest requirements on manufacturing technology. PDP processing relies on both thin and thick film deposition tools. Compared to TFTLCDs, which use photolithography and high-temperature processes in clean rooms, PDPs can be manufactured in less clean factories using low-temperature and inexpensive direct printing processes. Full colour plasma displays have long lifetime; typically 10,000 to 30,000 hours of life until they degrade to half luminance.

The DC-PDP operation is similar to its AC counterpart. However, in a DC panel, the electrodes are directly exposed to the discharge space and insulating barriers separates each discharge cell. Therefore, each discharge cell is essentially a miniature Neon tube with an anode and a cathode. To excite the gas, a voltage must be applied between a cell's anode and cathode, which exceeds the ionisation voltage of the gas. Using this method, a time lag is present between the application of the voltage and the activation of the cell. This can be overcome by using a priming discharge arrangement. Similar to a pilot light, this voltage is always maintained across each cell and reduces the time required before light is emitted.

Microdischarge Light Sources

The Microdischarge is at the heart of the new class of emissive plasma displays. Microdischarge is the term used to denote a class of gas discharges where the spatial dimensions are of the order of or less than 1 mm. These are hybrid solid state-gas devices with characteristics quite distinct from conventional macroscopic discharges [Bitzer 1966].

A planar glow discharge has three main regions. Electrons are accelerated in the cathode sheath, which is the first region. Beyond this the negative glow region, where electrons lose energy. The third region is the positive column, which connects the discharge to the anode. In a planar discharge, the negative and positive columns are spread over considerable length, which limits the power density of the discharge.

Microdischarges are short discharges without a positive column. The inter-electrode gap is typically 100 microns. In order to increase the secondary electron emission, the electrodes are coated with a dielectric layer of magnesium oxide. The gas mixture is at a typical pressure of 500 torr and consists of mixtures of Helium or Neon buffer gas with a small percentage of Xenon. The buffer gas facilitates breakdown while Xenon provides the ultraviolet light. The negative glow region is related to the cathode region and the excitation and ionisation are controlled by the high energy electrons emitted by the cathode. The microdischarge has a characteristic duration of 100 ns. The radiation efficiency of the microdischarges is rather low, typically several per cents. The plasma dynamics inside these microdischarges have been simulated in macrodischarges, typically with dimensions of tens of millimetres. The scaling up by a factor of 60 satisfies similarity laws

[Callegaris 2000] and the time and space dependent plasma phenomena to be more resolved. The light emission first appears on the anode and moves towards the cathode. Light emission is periodic, presumably driven by ionisation instabilities. The charging of the dielectric surface produces an electric field large enough to heat electrons to energies above the gas excitation thresholds [Punset 1999].

In contrast to the open discharge configurations now commercially used in PDP devices, new developments in fabrication techniques in VLSI and MEMS technology look very promising for building new types of microdischarges. A hollow cathode discharge is a subclass of glow discharge and offers characteristics quite unique from that of a planar cathode. In HCD, the cathode is a hollow cavity and the negative glow region is folded within the interior of the cavity. The electrons bounce back and forth between the opposing walls. HCD has increased current density and operates at lower voltages.

The theoretical upper limit of pressure for HCD operation represents a transition to normal glow discharge where the negative glow region will shrink within the cathode and the electron bouncing will stop. The product of pressure and interelectrode distance, which can be of the same order of the cavity diameter, the similarity parameter in gas discharges, is of the order of 7.5 torr cm [White 1959]. Hence with the reduction of the cavity dimension, the operating pressure can be increased. In the micron level the operating pressure can approach one atmosphere. This is good since the smaller size increases the resolution of the discharge panel.

Silicon based Microdischarge devices were reported in 1998 [Frame 1998]. This early device comprised of a Silicon hollow cathode 200 µm in diameter, a 1 mm thick dielectric and a thin metal anode. Stable glow discharges were produced in these devices at pressures as high as one atmosphere. Microdischarge devices with planar electrodes were subsequently fabricated and characterised [Frame 1988].

With the advent of photolithography and precision etching techniques, hollow cathode arrays of identical dimensions with inverted square pyramidal cathodes, point cathodes etc. have been fabricated [Chen 2002]. The pyramidal devices are characterised by positive impedance over the abnormal blow operating range [Park 2002]. Hence external ballasts may not be required for operating the array. The dimensional control afforded by micromachining allows single HCD smaller than 50 µm to be fabricated and operated above 1 atm. Large arrays producing uniform emission is possible. Fabrication costs for large arrays can also be reduced.

One of the most critical issues in PDP development is the improvement in luminance and luminous efficiency [Sobel 1998], which is dependent upon gas mixture composition, phosphor efficiency, driving voltage characteristics and cell geometry. Light generation efficiency defined as ratio of energy spent in excitation of UV emitting states per unit volume and unit time to the dissipated electrical power is an increasing function of the Xenon concentration [Veronis 2000].

The microdischarge is an extremely complex phenomenon due to the interaction of the surface with the plasma. They are also difficult to diagnose and characterise the microscopic details because of the size. Hence extensive computer models of the discharge have been developed which relate the physical phenomena with the parameters.

Thee are two modelling approaches. In the fluid approach, the plasma particle species are represented by macroscopic quantities such as particle number density, flux, mean energy etc. the space and time variation of these quantities is described by fluid equations, which are derived from the Boltzmann equation. Surface processes are accounted for in the boundary conditions of the fluid equations. The fluid equations are coupled to the Maxwell equations, which describe the electrical phenomena. In this way a self-consistent description of the discharge properties and their evolution is obtained. Unfortunately, the fluid equations and the boundary conditions incorporate restrictive assumptions concerning the particle transport. In addition, they require input data on macroscopic properties like diffusion coefficients, reaction rate coefficients etc. Due to these the fluid approach can be applied only to a limited range of discharge conditions.

More details are obtained by using a particle approach. In these models, the path of individual particles is followed by applying the forces acting on the particles. Since it is not feasible to calculate the path of all the particles, only a limited number of test particles are followed. To calculate the electric field self consistently, the particle models employ rather complicated techniques like the particle-in-cell method.

The two approaches can be combined in the hybrid models, where the bulk plasma is treated by the fluid method and the high energy electrons are treated by the particle method.

Market Drivers

Flat panel displays have a market in applications where minimum thickness is essential to the product [Fig. 15.4]. PDP technology and market development, therefore, has been aimed at displays for laptop and personal computers, wall hanging TVs, high definition television (HDTV), and large screen military and control systems applications. These areas have been supported by progress in semiconductor technology, and by advances in materials and fabrication techniques aiding compactness and weight reduction.

Televisions made up only a quarter of PDP sales in 2000. By 2006 it is predicted that this figure would increase to 77 per cent with the sales increasing from 100,000 units to 4.9 million in 2007 [EBU 2002]. The earlier segmentation of the flat panel display, with LCD screen sizes upto 30 inches and PDPs dominating in the larger screen size upto 61 inches is disappearing. With the LCD developments in the larger sizes there is a convergence. A comparison of operating features of LCD and PDP is given in table 15.1.

Among the many drivers for alternative non-CRT display devices, the high definition television- HDTV- has been a major one. The bright, high definition pictures in this mode would have no impact on the viewer, unless displayed on large screens of at least 1000-mm diagonal where all the details will be appreciated. They also demand much higher resolution than what is available in CRT's.

Cost is one of the major disadvantages of plasma display technology; prices for a 20" plasma display is roughly four times that of a conventional TV. In 2002 the price of a 42 inch PDP was $ 7600. These models from competitors are already being priced at less than $ 3,000. Prices are expected to fall by 20 per cent annually for the next few years [Time 2002]. The costs are contributed by two major areas; panel costs and driver costs [Weber 1999]. The panel cost now exceed the circuit cost but will come down when manufacturing volumes increase. The panel and circuit being complementary, the cost reduction can be significant with advancing technology. The key to the development of production techniques is consumer demand for the devices. As HDTV technologies become of greater interest to consumers, the production of this type of display should increase dramatically.

Several manufacturers such as NEC, Fujitsu, Matsushita Hitachi, Mitsubishi and Pioneer have already established production facilities. Plasma panels are emerging as one of the latest devices to fulfil large-scale display function. The major world players in display technology are Fujitsu, NEC, Mitsubishi, Toshiba and Plasmaco; all Japanese companies; Philips of Netherlands, Thomson Tubes Electroniques in France; Plasmaco, ElectroPlasma and Photonics in US and a number of Korean and Taiwanese companies.

The development of flat panel displays is a fast moving field with new ideas coming to light continually. Future work will be aimed at increasing panel size and luminance while lowering the voltage requirements. Much research will go into materials and manufacturing techniques, gas compositions to enable high luminance displays, and lowering costs. Flat panel displays are also entering other applications as shown in fig. 15.5. There is much room for advancement in the field of flat panel displays, and only time will determine as to which of these devices would take the biggest piece of the FPD pie.

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Table 15.1: Comparison of LCD and PDP displays

Technology	Advantages	Disadvantages
PDP	Plasma discharge technology established Wide viewing angle Rugged and reliable Simplified driving circuit Low cost high volume production possible Colour is feasible Long life time	High voltage driver Washout in bright sunlight Resolution limited
TFT LCD	Low driving voltages Very thin display Readable in direct sunlight Advanced technology	High processing cost Defect free TFT panels difficult to manufacture High capital equipment investment Low transmittivity of colour filters require strong backlight polariser set required

Fig. 15.1. The cathode ray tube

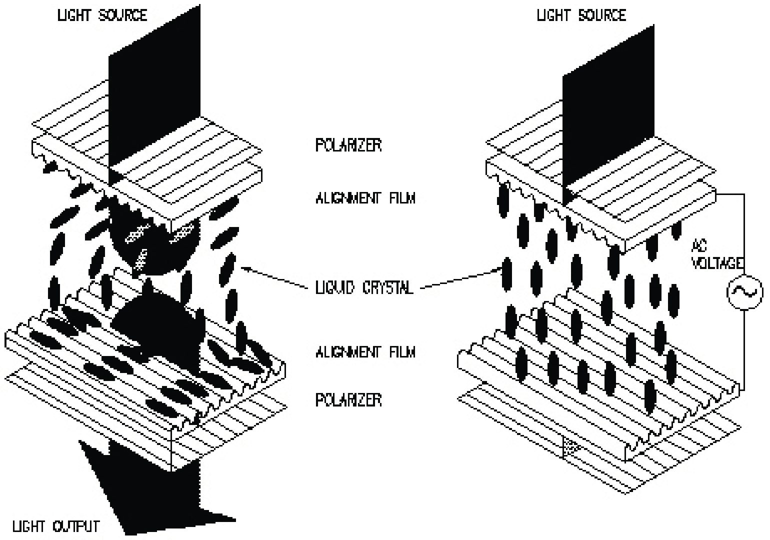

Fig. 15.2. The liquid crystal display

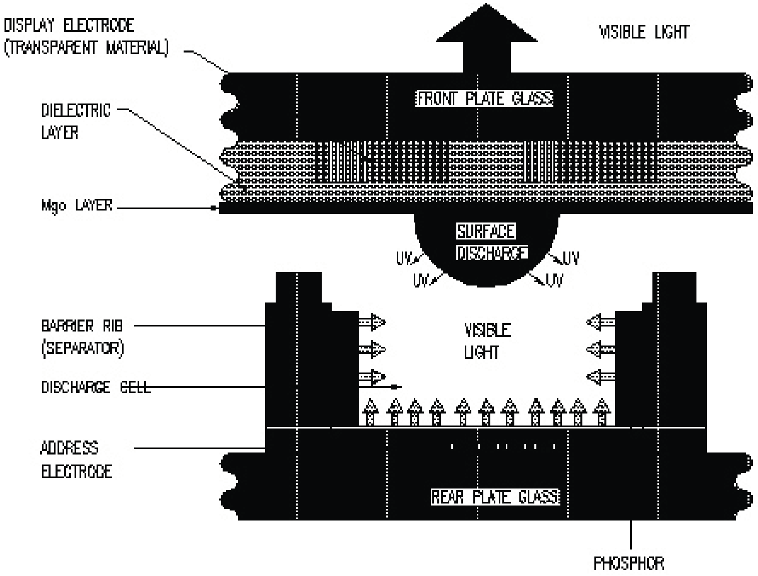

Fig. 15.3. Schematic diagram of an AC plasma display pixel

Fig.15.4. Photograph of a Plasmaco plasma display panel with a 60 inch diagonal screen (Photograph courtesy of Larry F Weber, Plasmaco)

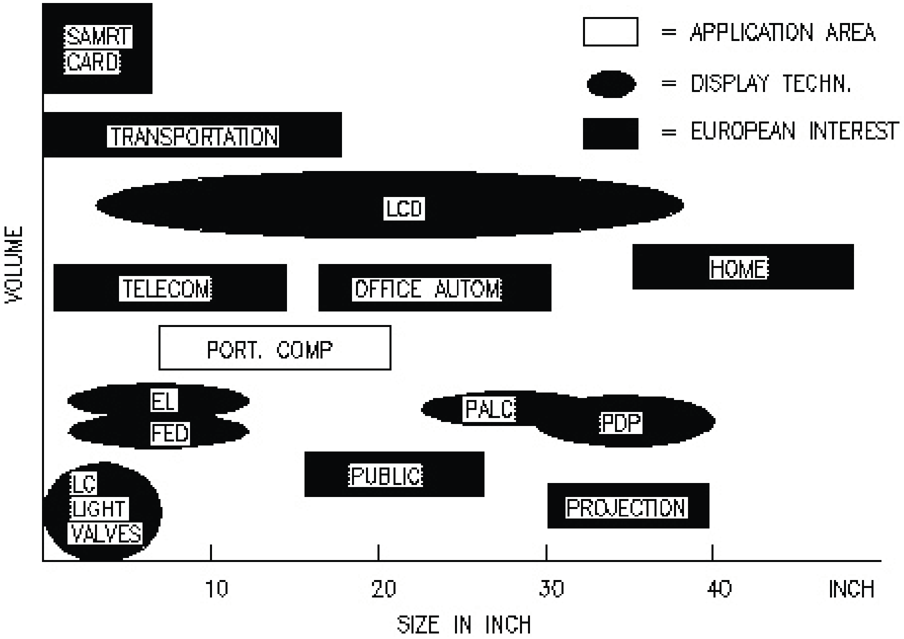

Fig. 15.5. Widening application areas of flat panel display devices

16. Clearing the Air

Plasma Remediation of Air Pollution

Air pollution is a major problem accentuated by increasing urbanisation and industrialisation. The major sources of air pollution are automobiles, fossil-burning power stations and petrochemical industries. New techniques of using non-equilibrium plasma techniques to clean up emissions and improve the environment are described in this chapter.

Anthropogenic Emission Sources

In the early morning hours of December 3, 1984, an estimated 8,000 people died in the north Indian city of Bhopal, choked by the accidental release of methyl isocyanate from the nearby Union Carbide C plant. Over 300,000 more continue to suffer from the exposure to the poisonous gas. The Bhopal gas tragedy has come to symbolise catastrophic effects of environmental damage by industrial sources.

Clean air is a delicately balanced mixture of Nitrogen and Oxygen, with small amounts of Argon, Carbon dioxide, Neon, Helium, and other gases. Pollutants such as ozone, aerosols, nitrous oxide, carbon monoxide and heavy metals poison this mixture, posing health risks to everyone who breathes the air. The effects on human beings have ranged from respiratory symptoms and illness, impaired lung function, hospitalisation for respiratory and cardiac diseases to increase in mortality. More people are estimated to die prematurely from lung disease every year due to particulate air pollution than from automobile accidents. Children are particularly susceptible to the effects of air pollution. Unborn babies suffer as carcinogens can be transferred from the mother to the foetus.

Air pollution is not necessarily a consequence of industrialisation. In developing countries, the most important source of emission is the burning of solid biomass fuels for cooking and heating. Pollution from natural sources occurs as a result of Methane emission from paddy fields and from livestock and forest fires.

Coal-burning power stations, motor vehicles and chemical industries are the primary source of urban air pollution. The combustion of fossil fuels is the principal source of emissions of fine particles. Automotive exhaust contains hydrocarbons, nitrogen oxides, sulphur dioxides, particulate matter, and carbon monoxide. Other dangerous emissions from vehicles include toxic organic compounds such as formaldehyde, acetaldehyde, and benzene. Chemical industries produce volatile organic contamination. Recent evidence suggests that diesel engine emissions are more dangerous than were previously considered.

Aerosols are mixtures of microscopic solid particles and liquid droplets in the air. Suspended particulate matter includes all air-borne particles in the size range from 0.5 to 100 microns. SPM less than 10 micron in size can pass into the human respiratory system.

Nitrogen dioxide and related Nitrogen oxides are produced when fuel is burned in power plants and motor vehicles. Nitrogen dioxide is a strong oxidising agent that reacts in the air to form corrosive nitric acid, as well as toxic organic nitrates. Ozone, the highly reactive form of oxygen, is formed in the atmosphere by the action of sunlight on nitrogen oxides and reactive hydrocarbons, emitted by motor vehicles and industrial sources. It also plays a major role in the production of smog.

Carbon monoxide is a poisonous gas formed by incomplete combustion of coal, wood, charcoal, or petroleum. In cities, automobile exhaust can cause as much as 95 percent of all carbon monoxide emissions. Other sources include industrial processes and fuel combustion in boilers and incinerators.

Sulphur dioxide is formed when sulphur-containing fuel, mainly coal and oil, is burned, primarily in power plants and diesel engines. Like nitrogen dioxide, sulphur dioxide can change in the atmosphere into acidic particles.

Waste incinerators emit fly ash, which can contain metals, including Lead, Nickel, Cadmium, Copper, and Mercury, as well as dioxins and furans. Particulate matter contains a variety of carcinogenic or toxic heavy metals, including Arsenic, Barium, Cadmium, Chromium, Copper, Iron oxides, Mercury, and others. Among the most pernicious airborne environmental threats is Lead.

Coal-fired power stations generate almost 40 per cent of the world's electricity - more than twice than from any other fuel. The environmental impact of fossil fuel burning is enormous. Emissions from a thermal power station can be carried many kilometres. Along the way the SO_2 molecules get transformed into sulphuric acid and the NO_x into nitric acid [Fig. 16.1]. They finally lash the earth as rain, sleet and snow. Acid rain, global warming, ozone depletion, and smog are thus some of the vexing environmental problems associated with fossil fuel burning.

Many countries are beginning to further strengthen the already stringent regulations to remove the pollutants at the source of emissions. For example, the 1990 Clean Air Act of US sets a permanent cap on sulphur dioxide emissions, restricting emissions nation-wide to 8.9 million tons per year after 2000. Stringent regulations are coming into existence in Europe and Japan also. The VOC directive in Europe published in 1999 is to prevent or reduce both the direct or indirect effects of volatile organic compounds emissions on the environment, mainly on air quality and to reduce potential risk to public health. The directive seeks to reduce European industry emissions by 57% in the 1990-2010 period. The regulation is estimated to affect 400,000 firms across 22 sectors of activity. The seriousness of the problem is beginning to be appreciated in rapidly industrialising countries in Latin America and Asia.

As newly industrialised nations increase their energy demands, world coal use is projected to double in the next 30 years. It is sobering to examine the emerging scenario of fossil fuel burning in two of the fastest developing economies, that of India and China. China, for example, now burns more than 1 billion tons of coal per year, one third more than a decade ago. India's coal use rose by almost 70 per cent in the 1980s.

India’s total power generation capacity is about 100 GW, with annual per capita consumption of electricity of about 300 kWh, which is far below the average of 8500 kWh of developed countries. Average electricity usage per person was 755 kWh and average household electricity usage per person was merely 72.7 kWh in 1994. Even among developing countries India’s consumption is only half of that of China. Coal is the primary energy fuel with nearly two thirds of power plants being coal fired plants. Coal is indigenous and plentiful and low in sulphur. Unfortunately, it contains a significant amount of ash, as high as 40-45 per cent. The main reason for coal’s dominance lies in the large reserves, which at current consumption rates should last for 240 years.

India has to add 10-15 GW every year to meet the rising demand from industry. This can be done through thermal power plants using coal, oil and natural gas. National Thermal Power Corporation, the biggest public sector power company in India is planning to increase production by 30 GW by 2007 [Singh 1999]. Experts predict that at least 60 per cent of the power produced in the next two or three decades will be dependent on coal. Present estimates of NO emission from thermal power stations are 13.1 gm/kWh with a total emission of 8,000 tonnes/day. The sulphur content of Indian coal being low, the computed value of SO_2 emission from all power stations is 7600 tonnes/day with an emission rate of 7.4 gm/kWh [OSC 2003]

Power industry in China has grown rapidly since the economic reform started in the 1980's. Coal is still the major energy source in China. The national average of sulphur concentration in coal is approximately 1.2 per cent and in some areas the concentration is as high as 5 per cent. In 1990, the total consumption of primary energy reached 987.03 million tons coal equivalent in China, of which 76.2 per cent was shared by coal. By the end of 1995, China's total generating capacity reached 217 GW, electricity generation was 1007 billion kWh and 74 per cent of this came from thermal power. This is more than a quarter of the total global coal consumption. With a newly installed capacity of 16 GW per year, by 2000, China's total generating capacity went up by 290 GW. Coal consumption for power generation will reach 600 million tons. By the year of 2010, it is expected that 1.9 billion tons of coal will be produced in China to feed the total installed generator capacity of 500 GW or higher.

According to China's National Environmental Protection Agency (NEPA), contribution to the acid rain from SO_2 is more than 10 times larger than that from nitrous oxides and in 1996, 40 per cent of China's total landscape was prone to acid rain. Nearly 85-90 per cent of the SO_2 emission comes from coal-fired power stations. In 1994, according to the Environmental Protection Office at the Ministry of Electric Power Industry, the smoke dust and SO_2 discharged by thermal power plants under the control of the ministry and with capacity of 6 MW or more, were 4 million tons and 5.81 million tons respectively. The economic loss from reduction of crop production, deforestation and degradation of public health, caused by sulphur dioxide and acid rain, was estimated at $14 billion in 1995 in 11 provinces in southern China. The annual economic loss in these areas, if SO_2 emission is not controlled, is expected to increase further.

Diesel engines are at present the most efficient vehicular propulsion systems. Heavy trucks and buses are powered almost exclusively by diesel engines worldwide. Diesel vehicles produce less carbon monoxide and carbon dioxide than their petrol burning equivalents, but they generate large amounts of Nitrogen and Sulphur oxides and soot as shown in Fig. 16.2. Diesel particulates have dimensions in the range of 0.1-10 microns which once emitted can stay in the atmosphere for a week and can be inhaled by human beings. In developing countries, 40-80 per cent of source of air quality crisis is often attributed to vehicular emissions [Ghose 2002]. It is estimated that 39 per cent of NO_x released into the atmosphere originates from mobile sources. Until now no durable catalyst for the reduction of NO_x in the exhaust gases is available [Kreuzer 1996]. The new 2004 emission standards in the US as well as the tightening regulations in Europe and East Asia reflect the growing concerns with diesel emissions. All over the world, diesel engines present a growing pollution hazard, as the number of diesel-powered cars and trucks continues to increase. According to the Society of Motor Manufacturers and Traders, 22.5 per cent of all cars in Western Europe were powered by diesel engines, compared to less than 6 per cent in 1989.

An advisory committee of the British Government, The Quality of Urban Air Review Group, estimates that on average a diesel car pumps out nearly double the amount of Nitrogen oxides produced by an equivalent petrol driven vehicle. Car and truck manufacturers are working on catalytic converters to reduce emissions of nitrogen oxides and sulphur dioxide, but there are no commercial models in the immediate horizon, according to the review group.

The booming consumerism has spurred the demand for multitude of consumer products. Volatile organic contaminants are the by-product of manufacturing processes for raw materials, intermediates or the final product. VOC sources are present as chemicals, solvents, release agents, coatings or decomposition disposals [Penetrante 1995]. In most manufacturing there is a gaseous effluent that contains low concentrations of organics. CFCs and PFCs are present in most industrial solvents, despite the ban against using them.

Compounds subject to regulation include toluene, methelyn chloride, perflourinated compounds such as nitrogen triflouride and sulphur hexaflouride, oxides of Nitrogen and Sulphur.

90 per cent of rural households in developing countries rely on unprocessed biomass for their fuel needs [UNEP 1998]. Incomplete combustion of biomass releases aerosols, CO, polyorganic materials, poly aromatic hydrocarbons (PAH), formaldehyde etc. [ICMR 2001]. Household cooking data for Ahmedabad shows that 100-150 mg of CO is released during cooking a meal using wood and coal. PAH constitute a large class of compounds released during combustion of organic matter. Benzo (a) Pyrene (BaP) is an important carcinogen of the group.

Nonequilibrium Plasma Processes for Pollution Control

Plasma-aided processes can play a significant role in mitigating the environmental impact of atmospheric pollution [Penetrante 1993]. It is generally recognised that the plasma produces an abundance of active species, which can produce a large range of reaction pathways than those available through traditional thermal activation.

In non-equilibrium plasmas, electrons have an energy distribution different from and not in equilibrium with that of the heavy particles. Thus, the electron gas can be assigned a temperature substantially higher than that of the heavy neutrals or ions. The high energy of the electrons is then preferentially directed to produce excitation, dissociation and ionisation by electron impact to produce radicals that in turn decompose the toxic molecules. Plasma chemical reactions can be targeted to transform specific species. Energetically this is a far more efficient way of using the plasma properties for the required transformation, in contrast to the use of the thermal energy of the plasma to break up the molecules by thermal dissociation. This is especially true in many practical applications where the toxic molecules form a dilute concentration. This has to be contrasted with the sledgehammer and fly approach of incineration.

Since the non-thermal plasma processes involve the ionisation or dissociation of the carrier-gas molecules (N_2 and O_2) via collisions with energetic electrons and subsequent interaction of radicals/ions with the target gas molecules; much of the electrical energy may be wasted in producing unused ions/radicals in the carrier gases. Therefore, Oak Ridge National Lab (ORNL) researchers believe that these non-thermal processes are not very energy efficient, even though they offer an improvement over thermal plasma processes. Hence, they are working to develop an innovative plasma chemical process that is based on extremely large electron attachment cross sections recently discovered at ORNL for the highly excited electronic states of molecular species. Furthermore, a discharge-based, target-specific excitation process is being investigated for the excitation of target molecules. The proposed approach exploits the new knowledge on electron attachment to highly excited states and the knowledge on excitation transfer from rare gas metastables. The ability of this process to "zero in" on target gases without wasting energy on the bulk of the carrier gases consisting of N2 and O2 should lead to significant cost savings.

Atmospheric Pressure Nonequilibrium Plasma Sources

Plasma application to pollution control will be meaningful and widely applicable only with the availability of devices producing non-equilibrium plasmas at atmospheric pressures. This is because of the high throughput requirements of the process to match the effluent flow rates in typical systems like a power station. Such plasma sources are based either on high energy electron-beam irradiation or electrical discharge methods. The latter category consists of pulsed corona, dielectric barrier, surface, and packed-bed corona discharges.

All atmospheric pressure nonequilibrium plasma discharges are based on techniques, which prevent the transition of glow discharge into an arc discharge. Electrical energy deposited into the discharge produces electrons with typical energy of less than 5 eV [Penetrante 1995], which gives them much higher average kinetic energies than the surrounding gas-phase ions and molecules. These energetic electrons can interact with the background gas to produce highly reactive species (i.e. radicals, anions, cations, and secondary electrons) that will preferentially destroy pollutants.

Many electrical discharges produce non-equilibrium electron population through the medium of micro discharges called streamers. Streamers are plasma filaments produced by highly localised space charge waves, which enhance the applied electric field in front of the wave and propagate by developing an electron avalanche in this field. Streamers yield good power efficiency since in the short lifetime of the streamer, the ions do not move and hence do not consume power. The short time of the streamer is achieved passively by shielding the electrode potential by the space charge or actively by the use of high voltage pulses with typically nanosecond duration.

The corona discharge is a high-pressure discharge, which develops in a non-uniform electric field. The non-homogeneity of the field can be obtained through small diameter of one or both electrodes. The electrode configuration is most often wire-cylinder, point-plane, etc. The current may be direct, alternating, or pulsed. The most frequently used pulse discharges use nanosecond pulses. Most of the electrical energy is used for the production of energetic electrons. The type of the discharge in a particular gas mixture depends on the electrode configuration and on the type of the current source. The active region develops clusters, which can be separated by an electric field. The efficiency of the process can be increased by atomised water or another suitable solvent, usually of an alkaline nature, used for neutralising of the acid constituents. By adding a ferroelectric material like Barium Titanate, which has a dielectric constant of the order of 15,000 in the gap between the electrodes, the electric field can be intensified increasing the corona efficiency.

The corona discharge in ecological applications is usually a system of corona discharge tubes connected in parallel physically as well as electrically which increases the flow through the system. The greatest advantage of apparatus of this type is that they are scalable to treat large flow volumes.

The catalytic layer, which develops at the electrodes, is more advantageous in comparison to the chemical catalytic layer. In the conventional catalyst, the electrons needed for the conduct of some chemical reactions are obtained chemically, i.e. by adding an appropriate electron donor to the “wash-coat” (e.g. an addition of MgO). In the electro-catalytic layer, these electrons are supplied by the discharge itself. This is a much more efficient way and the channels of the catalyst, which are identical with discharge tubes, may be much wider than in the conventional catalyst.

Two processes separate the products of the plasma-chemical reactions. Charged particles are separated electrostatically whereas the neutral particles are separated by convection in the electric wind. The size of the particles, which can be separated this way, ranges from 0.1 to 100 microns.

The supporting technology for the pulsed corona reactors is quite advanced. The electrically significant characteristic of the positive corona load is its non-constant impedance value vs. time and applied voltage, contributed by both resistive and capacitive components. When the applied voltage is above 80 kV a flat impedance zone appears from 200 to 600 nanoseconds. This has led to the developments of constant voltage pulse generators using pulse-forming lines.

If there is a dielectric or a ferroelectric material in the space between the electrodes, the breakdown charges the plasma boundary to the applied polarity, quenching the discharge. Application of a bipolar pulse to drive the discharges helps in clearing the space charge initiating another transient discharge. This scheme was first introduced by Siemens in the 1850s and goes by the name silent discharge. These discharges are routinely used for commercial production of ozone for applications such as water purification and textile bleaching. Combinations of pulsed corona and dielectric barrier discharges are also being developed in many laboratories. The material of the electrodes with the dielectric or ferroelectric layer develops a catalytic effect. Each of these discharges has its specific features and is effective for certain components. Effects, similar to those of the discharge with a dielectric layer, can be obtained with a DC discharge if water or other suitable medium is atomised in the discharge space.

A third non-equilibrium plasma route is the UV photochemical reactor, made possible by the advent of surface discharge plasma sources. This typically consists of a planar or cylindrical alumina or plastic surface having a series of strip like electrodes attached to one of the surfaces and a film-like counter electrode embedded inside the material. High voltage high frequency pulses produce breakdown on the surface, which become a copious emitter of energetic ultraviolet radiation.

Gliding arcs are arc discharges, which slide down a set of divergent electrodes in a gas flow [Lesueur 1979]. It acts like a plasma string, which heats the gas and produce excited species in the weakly ionised layer surrounding it. .

Processing of Power Station Emissions

The preferred role of plasma in power station application is to oxidise NO and SO and eventually convert the oxides into nitric and sulphuric acids. OH radicals produced in the plasma play the major role in simultaneous oxidation of NO and SO_2 to their respective acids [Matzing 1991]. Mixing ammonia with the acids produce the desired salts, which are removed by scrubbing.

The non-thermal plasma techniques originally entered in pollution control problems through the development of the Electron Beam Processing, where the energy of an electron beam permeating the gas to be treated is used directly to dissociate and ionise the background gas. During ionisation by the beam a shower of secondary electrons is produced, which further produce a cascade of ionisation and dissociation. This cascading produces large volume plasma that can be used to initiate the removal of various types of pollutant molecules.

The electron beam process is a dry scrubbing process [Fig. 16.3] and has been successfully applied in the removal of sulphur dioxide and nitrous oxides. Before entering the spray cooler, the flue gas is cleaned of fly ash by using electrostatic precipitators or other standard techniques. In the spray cooler the gas temperature is lowered, and the process water increases the gas humidity. The gas then passes through the process vessel where it is irradiated by beams of high-energy electrons in the presence of near-stoichiometric amount of Ammonia. The active species such as O, OH and HO_2 are generated by the beam irradiation. The SO_2 and NO_x are oxidised and converted into their respective acids and these acids are subsequently converted into ammonium sulphate and ammonium nitrates and removed by electrostatic precipitators. The by-product can be used as fertiliser and the clean gas is released to the atmosphere. The electron beam process has been assessed for operational and capital cost in comparison with the conventional wet limestone process and has been found favourable with $ 215/tonne of SO_2 removed.

The Ebara Corporation in Japan initiated the Electron Beam Ammonia (EBA) process in 1970 and in collaboration with the Japanese Atomic Energy Research Institute (JAERI) set up a 60 N m^3/h test facility which tested gases with concentrations of 900 PPM of SO_2 and 80 PPM of NO_x.

Subsequent to this, Ebara, in a joint effort with Nippon Steel, the NOx Association and others built and tested a 10,000 Nm^3/h flue gas plant at Wakamatsu to remove SO_2 and NOx from the exhaust of a steel sintering plant. The result was NOx removal at over 90 per cent and SO_2 removal at over 95 per cent. In 1992 a 12,000 Nm^3/h coal burning facility was also built by Ebara Corporation in Nagoya, with the purpose of demonstrating the process over a wide variety of fuels. A 300,000 Nm^3/h plant was commissioned in Chengdu in China in 1997. The capital cost of the EBA process is $ 150-200/kWe, which is considered competitive to other processes. The operating cost is estimated at $ 635/ tonne removal.

US efforts in this field started with a programme by Research Cottrell sponsored by the Department of Energy (DoE) in 1979-80. In 1984 Research Cottrell built a pilot plant at the TVS Shawnee Steam Plant and conducted tests towards producing sulphuric and nitric acids, which got converted into calcium sulphite and calcium nitrate using an alkali slurry spray of hydrated lime. Ebara Corporation, in collaboration with DoE embarked on a programme to build and operate a plant at the Indianapolis Power and Light Company's E. W. Stout Plant in Indianapolis.

The International Atomic Energy Agency (IAEA) has supported setting up of a 300,000 m^3/h E-beam treatment system in 1999 at the Pomorzany power station in Poland [IAEA]. This is based on a pilot plant at Kaweczyn, which achieved a removal efficiency of 90 per cent for SO_2 and 70-90 per cent for NO_x. The process has been proven to be competitive to other techniques.

The electron beam technology has made rapid advancement in the recent years, primarily spurred by the requirement of inertial confinement fusion research programmes. Developments such as large scale saturable magnetic switches, high peak-power linear induction voltage adders and large area electron beam diodes took place for fusion programme. With the improvements in thermal management techniques and an understanding of reliability issues, pulsed electron accelerators are good candidates for high average power industrial applications. However, the high capital cost of the electron accelerators and the x-ray hazard associated with electron beam techniques have motivated studies into alternate plasma based technologies such as those utilising electrical discharges in high pressure gases.

The Italian National Electricity Board (ENEL) has pioneered the work on pulsed Corona treatment of flue gases. The main steps in their process are:

- Production of free electron in the 5-20 electron Volt energy range
- Production of radicals O, OH, HO_2, N
- Partial conversion of SO_2 into H_2SO_4 and NO into HNO_3, NO_2 and N_2.
- Injection of ammonia to convert acids into ammonium salts
- Collection of the salts in an electrostatic precipitator.

The ENEL technology is attractive because of the prospect of simultaneous removal of NO_x and SO_x with a single dry process. The process can be based on existing electrostatic precipitators and the by-product can be used as fertiliser. In 1988 ENEL set up an industrial scale facility at Marghera, Italy with power consumption, which was 5 per cent of the electricity generated by the plant. A study committee sponsored by the Japanese Ministry of International Trade and Industry (MITI) through the Japan Association of Machinery Industry has recently assessed the Pulsed Corona Process for coal-burning utility boilers. The PC process was compared to the conventional calcium-gypsum process for $deSO_x$ combined with the ammonia catalytic process for $deNO_x$ as well as with the electron beam route for $deNO_x/deSO_x$ process. The study committee concluded that PC method deserves development as the next generation technology for the removal of SO_2 and NO_x in utility boiler plants.

Cleaning Diesel Engine Exhaust

Increasing environmental awareness and regulatory pressures are the drivers for finding energy efficient methods of removal of nitrogen oxides and particulates from diesel exhaust. The air-fuel ratio in the internal combustion engine has a marked effect on the emission of hydrocarbons; as the ratio becomes leaner with stoichiometrically less fuel, the emission decreases. Improvement in diesel engine performance appears to have reached a plateau and some form of after treatment seems to have been necessary. Diesel particulate traps suffer from the requirement of continuous regeneration to avoid uncontrolled burn of the accumulated particulates. Conventional catalyst technology is ineffective under the lean burn conditions. The emerging technology is to combine plasma techniques with catalysts without the use of additives. In contrast to power plant application, nonthermal plasma techniques in treating vehicular emissions have to initiate NO_x reduction to avoid the need for scrubbing the process products. This is not trivial since the engine exhaust is a highly oxidising environment. Conventional catalytic converters are ineffective in the Oxygen rich atmosphere. Non-thermal plasma techniques could presumably initiate NO_x reduction chemistry similar to those of thermal or catalytic deNO_x methods.

Plasma interaction with NO_x in the presence of N_2 and O_2 leads primarily to oxidation. The electron kinetic energy is deposited preferentially into the major constituents. The electron impact dissociation can produce highly reactive N and O radicals. At the typical electron temperature of 3-6 eV available in nonequilibrium plasma sources [Penetrante 1995] the dissociation of O_2 will dominate over the dissociation of N_2. The oxidation reaction converting NO to NO_2 becomes less and less efficient as the temperature increases, because of the reduction reaction

$$O + NO_2 \rightarrow NO + O_2$$

In the hot environment of the engine exhaust at typically 300^o C, it has been shown that only 10 per cent of NO is oxidised in a stream of 500 ppm NO in 10 per cent O_2 and balance N_2. However, in the presence of 1000 ppm C_3H_6, the conversion efficiency increases to more than 80 per cent. This is attributed to the consumption of Oxygen radicals in reactions with hydrocarbon molecules. Thus, the presence of hydrocarbons appears to be critical to plasma oxidation of NO in hot engine exhausts. The plasma oxidation in conjunction with selective catalytic reduction by hydrocarbons leads to plasma assisted catalytic reduction of NO_x. This is accomplished in the following two steps:

$$\text{Plasma} + NO + HC + O_2 \rightarrow NO_2 + \text{HC products}$$
$$\text{Catalyst} + NO_2 + HC \rightarrow N_2 + CO_2 + H_2O$$

Figure 16.4 is an illustration of how the process works. A pulsed corona discharge produced by a coaxial wire and cylinder geometry is located upstream of the catalytic reactor. Propane is used as the hydrocarbon reductant. The infrared spectra of the emitted gas show how the combined action of the plasma and catalyst reduces NO_x efficiently.

AEA Technology in the UK, associated with the UK fusion research laboratory at Culham, has developed the Electrocat Diesel Particulate Filter for cleaning up the particulate emissions from diesel exhausts. Early trials were carried out at Southwest Research Institute (SwRI), processing diesel exhaust from Dodge and Toyota diesel pickup trucks. The reactor employs AC voltage applied across a ceramic pack material. The pack material increases the residence time of the particulates significantly, allowing complete oxidation at modest cost of energy of the order of 0.34 kWh/g [Thomas 2000].

Simultaneous particulate removal up to 90 per cent and NO_x reduction up to 75 per cent have been demonstrated.

Plasma automobile exhaust cleaning systems have to operate within strict energy consumption budgets to be industrially acceptable. The electrical energy consumption of different types of nonthermal plasma sources such as pulsed corona, dielectric barrier and dielectric pellet reactors used in treating NO diluted in N_2 is about 240 eV per NO molecule. This common value is attributed to the shielding of the electric field seen in all such devices [Penetrante 1995]. Alternators on most modern cars produce up to 100 kilowatts of electricity at high speeds and between 20 and 25 kilowatts at normal coasting speeds. The goal is to achieve 90 per cent NO reduction at 5 per cent engine power. Electrocat claims consumption of 1 per cent engine power.

Destruction of Volatile Organic Contaminants

The ability of non-thermal, low-temperature plasmas to destroy relatively low concentrations of VOCs at atmospheric pressure is well known [Scheytt 1993]. Interest in these technologies has grown recently due to the increasing stress on global pollution control and environmental remediation activities. Low temperature plasmas are particularly attractive for treatment of low-level waste concentrations and for dealing with compounds that resist treatment by standard chemical means. One important class of these compounds is halogenated compounds such as carbon tetrachloride (CCl_4), trichloroethylene (C_2HCl_3) and hexaflouroethane (C_2F_6). The destruction and treatment of such compounds is particularly important since some of the chlorinated solvents were used for decades in a wide variety of processing applications. For example, CCl_4 has been used extensively in the chemical processing of irradiated nuclear materials and discharged over many years. Contaminated spots contain ~ 8000 ppb of CCl_4 in the groundwater which greatly exceeds the drinking water standard of 5 ppb.

There are three basic types of chemical reactions responsible for the decomposition of VOCs. The electron impact dissociation of oxygen molecules produce O and OH radicals (if water vapour is present) that can oxidise the VOC molecule through the reaction:

$O^* + CCl_4$ ®$ClO + CCl_3$

The low energy electrons produced in the plasma can decompose VOC molecules via dissociative electron attachment as in:

$e + CCl_4$ ®$Cl^- + CCl_3$

The plasma ions can decompose the VOC molecule via dissociative charge exchange through the reaction:

$N_2 + CH_3OH$ ®CH_3+ $+ OH + N_2$

Destruction of large inventories of halogenated solvents clearly relies upon the development and deployment of effective and efficient treatment methods. In packed-bed coronas, the high frequency of surface collisions involving reactive and/or energetic species suggests that surface mediated processes could also affect the overall plasma efficiency. The synergism between the electron-induced plasma chemistry and surface reactions can be exploited in the treatment of waste streams as well as in reduction of nitrogen oxides in highly oxidative combustion exhaust streams.

Corona discharges have been tested for a broad range of compounds. They were highly efficient with the following compounds: CO_2, NO_x, SO_2, HCl, HF, H_2SO_4, chlorohydrocarbons, dioxins, phenols, NH_3, SiF_4, heavy metals in the form of organo-metallic compounds (Arsenic, Lead), organo-phosphoric compounds etc. Volatile organic compounds such as benzene, styrene, xylene, toluene, methyl- and ethyltoluene, methyl- and ethylbenzene, ethyl- and butylacetates, cumol, mesitylene, phenol, methylene chloride, trichlorotrifluoroethane, petrol, as well as commercial solvents, mainly the nitrocellulose have also been remediated. The decomposed original compound in the form of a radical is subject to polymerisation or copolymerisation, which results in the development of an aerosol consisting of polymeric granules of very small size.

The ability of nonthermal plasma to mitigate volatile organic contaminants is also finding increasing application in the treatment of in-door air pollution. A very interesting spin off of this technology is the air treatment of closed systems like spacecrafts on long duration space missions. Current technologies use Carbon to filter out contaminants in air circulators used in such systems. However existing Carbon adsorbing systems are inadequate to take care of extended missions, because of the saturation of the system and the requirement for regeneration. One specific problem in such missions is the need to nurture plant growth for the production of food in-situ. Ethylene gas, which is produced in such environments, has to be destroyed to mitigate their negative effect on plant growth. The work on nonthermal plasma sources based on capillary type discharges being pursued at the Stevens Institute in New Jersey has been applied to such conditions [Christodoulatos 2000] as well as to terrestrial applications such as elimination of VOCs from contaminated soil and ground water. These applications have been commercialised by Plasma Sol Corporation, a company spun off from Stevens.

Troposphere Washing

The conceptual demonstration of the potential of plasma based techniques to attack environmental problems on a truly global scale is another recent development. The destruction of the ozone layer by chlorofluorocarbon pollution of the upper atmosphere is one such problem. Emission of CFC compounds (CF_2Cl_2, $CFCl_3$) from earth passes through the troposphere and reaches the ozone layer (> 15-20 km). The photo dissociation of CFC by sun's ultraviolet radiation produces Chlorine, which destroy ozone through reactions such as

$Cl + O_3$ ®$ClO + O_2$

CFC can also influence the global heat balance, as one CFC molecule is equivalent to 10,000 CO_2 molecules. Although CFC is now banned from manufacturing, large amounts have already been released into the atmosphere, where they are likely to stay for long time. The residence time of CFC-12 is 110 years and that of CFC-13 is 90 years.

Many ideas have been put forward to remediate this problem. The basic approach is to dissociate CFCs before they reach the vulnerable heights. The Chlorine formed in the dissociation become negatively charged and do not take part in the catalytic reactions, which destroy ozone. Stix proposed a CO_2 laser based resonance multistep photodissociation of CFCs, which was limited to near earth heights since it needed mirrors to reflect the laser light back and forth [Stix 1991]. Radio frequency heating of the ionosphere above 40 km [Wong 1989] is also ineffective as the hot electrons are produced far away from the location of CFC's.

Stenflo et. al [Stenflo 1994] have recently proposed irradiating the CFC region by intense pulsed microwaves to produce a free standing discharge in the troposphere. The electrons produced in the discharge would dissociate the fluorocarbon molecules. The pulsed power required is few gigawatts and is probably available from gyrotrons or relativistic magnetrons. A scaled down experiment using gas at 500 torr and microwave power of 60-100 kW at 0.8 cm and 300-500 kW at 2.5 cm. has demonstrated the feasibility of the concept. The plasma thus formed is highly non-uniform with filaments and striations. An unexpected observation was that the plasma lifetime was anomalously long and could not be explained by available attachment and recombination data.

Decarbonisation and Fuel Reforming

In contrast to the "end-of-pipe" approaches described above, where consumers and industries generate waste, which is sent outside for processing, an alternative approach is currently gaining ground. This approach is more holistic from the viewpoint of resource utility and waste minimisation. This is also consistent with the historical reality that the fuels we use have gradually moved away from those with high concentrations of Carbon relative to Hydrogen, such as coal, to those with lower Carbon contents, like oil and then to gas. This movement is expected to continue as new fuels, such as Hydrogen and energy from renewable resources, get cheaper and become more available.

Until about the year 1800, the energy system relied on Carbon. Wood, the traditional energy material burns about 10 Carbon atoms for each Hydrogen atom. Carbon is a dirty element as fuel since it becomes soot or carbon dioxide. Hydrogen becomes water after burning and hence is a clean one. For the past 200 years, the world has progressively favoured Hydrogen atoms over Carbon. Coal approaches parity with one or two C's per H, while oil is better with 2 H's per C. Molecules of natural gas, CH_4, are abundant in hydrogen. The trend towards decarbonisation shown in fig. 16.6 is a part of the evolution of energy systems [Ausubel 2000].

Plasma technology could provide new methods in washing carbon from hydrocarbon fuels for the production of hydrogen-rich gas; a process known as fuel reforming [Bromberg 1997, 1998]. This is realized in a device developed at MIT called 'plasmatron fuel converter' schematically represented in Fig. 16.7. Non-equilibrium plasma can be created in flowing gases of hydrocarbon fuels and air to accelerate thermodynamically favorable chemical reactions without a catalyst or provide the energy required for endothermic reforming processes. The generation of reactive species in the flowing gases along with increased mixing accelerates reforming of hydrocarbon fuels into Hydrogen rich gas.

Plasmatron fuel converters work with a DC arc as well as with low current discharges. The latter allows operation at much reduced plasma power relative to arc plasmatron fuel reformers and produce nonthermal plasma, with electrons are at much higher temperatures than the ions and neutrals, which are at near room temperature. The relatively large area electrodes produce a discharge over a large volume. The power consumed is in the range of 300W to 600W. The Hydrogen conversion efficiencies as a function of the energy consumed is shown in Fig. 16.7.

This type of low current devices has been used to convert natural gas, gasoline and diesel fuel [Cohn 1998] into Hydrogen rich gas. In the partial oxidation mode, typical power conversion efficiencies, defined as the ratio of heating value of the product gas to heating value of the fuel were 60-85 per cent. Diesel fuel streams with chemical power levels of 5 to 20 kW have been processed into hydrogen rich gas. Soot production, the bane of the diesel fuel was minimal, even after extended operation. At oxygen/carbon ratios of 1.2-1.5, and fuel rates of 0.3-0.5 g/s, which corresponds to about 10-20 kW of fuel power, high concentrations of Cydrogen and CO are obtained. The startup yield of hydrogen with both diesel and gasoline was 30 per cent, increasing to 80 per cent after 90 seconds. The startup power conversion efficiency of 30 per cent increases to 70-80 per cent after warming up.

A Spark ignition engine can access the extra lean operation regime with hydrogen rich fuel. A Hydrogen rich gas significantly increases flame speed, thereby extending the lean region of engine operation without misfire. A Very lean operation substantially decreases emissions and improves efficiency [Breashers 1973]. For NO_x reduction in a spark ignition engine, the Hydrogen rich gas produced by processing a fraction of the fuel in a fuel converter is injected into the cylinder as an additive. This mixture facilitates diluted engine operation, with either very lean or heavy exhaust gas recirculation mode of operation. The thermal capacity of the air/fuel mixture increases by this dilution, decreasing both the peak combustion temperatures and NO_x emissions. This approach is particularly attractive in state of the art gasoline and natural gas engines where only a relatively modest amount of Hydrogen may be necessary to allow very lean operation without any misfire [Bromberg 1999]. Substantial increases in overall efficiency in spark ignition engines may be possible using fuel converter coupled with the engine. It is speculated that with high conversion ratios and optimization of the engine for very lean, high compression ratio, open throttle operation spark ignition engines could approach the efficiencies of a diesel engine. The net efficiency will, however, be lower because of the power loss due to plasmatron fuel converter operation [Bromberg 1999].

Fuel converters can also remediate NO_x emissions [Fig. 16.8]. An absorber catalyst in the diesel engine exhaust can be used for trapping the NO_x and then be regenerated by the use of highly reducing Hydrogen and CO from the plasmatron fuel converter. Experimental studies of combined SO_x and NO_x traps [Parks1999] examined both the use of diesel fuel and hydrogen as reducing agents for trap regeneration and have claimed a 98.9 per cent reduction in NO_x and Hydrocarbon (HC) emissions from diesel engines. NO_x and HC have been reduced to 0.4 grams per brake horsepower-hour, an emission reduction that is an order of magnitude lower than the U.S. EPA's 2002 emission reduction requirement. A similar process may be used for particulates also. The particulates can be trapped in one system, and then released and treated in a downstream unit (engine or another catalyst).

This chapter started with remembering one of the worst human tragedies wrought by runaway industrial pollution. It can end on a hopeful note by remembering that human creativity can also find solutions to these problems. Plasmatron fuel converter is indeed a symbol of such creativity.

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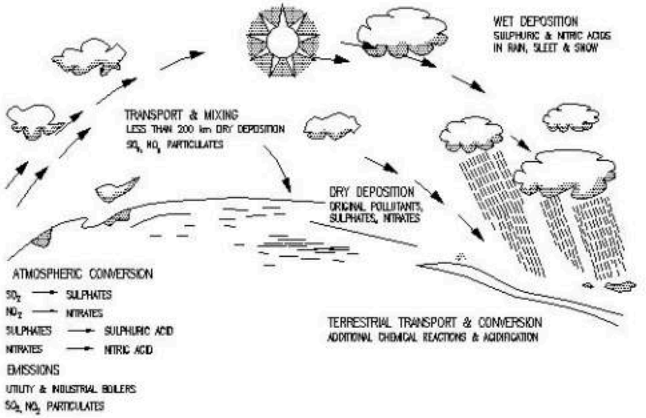


Fig. 16.1. Atmospheric transport of pollutants from the sources of emission

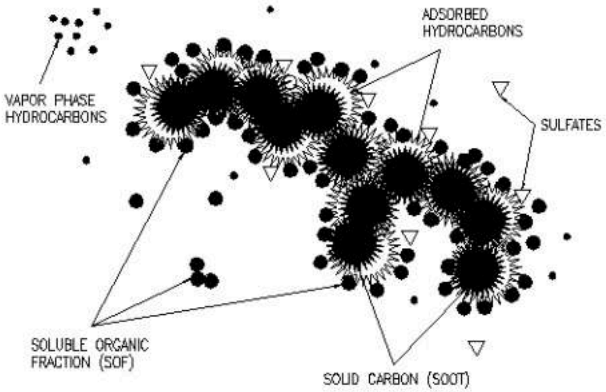


Fig. 16.2. Characteristics of particulate emissions from diesel engines

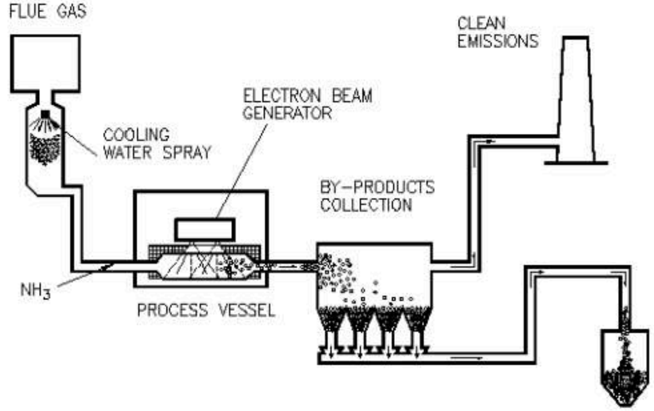


Fig. 16.3. Schematic diagram of electron beam process for dry scrubbing of flue gases

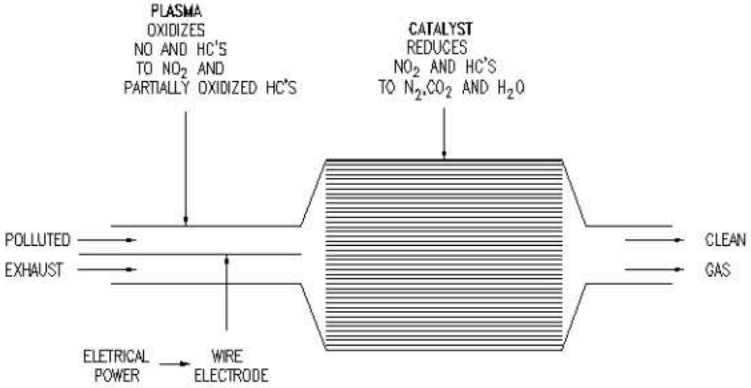


Fig. 16.4. Corona based plasma remediation of NO_x emissions

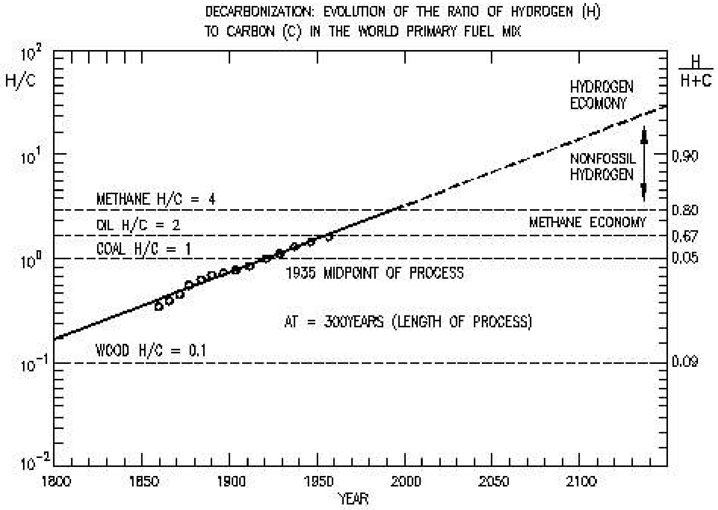


Fig. 16.5. Trends in decarbonization of fuels (figure courtesy of Prof. Jesse Ausubel, Program for the Human Environment, The Rockefeller University, New York

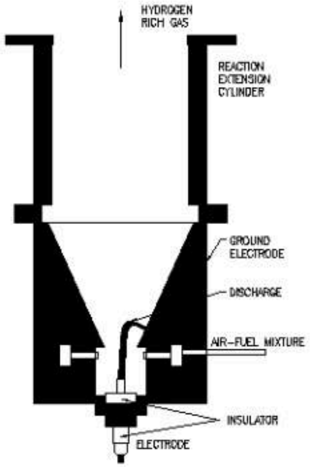


Fig. 16.6. Plasmatron fuel reformer invented by MIT scientists (Figure courtesy of Prof. Daniel Cohn, MIT and SAE International, USA

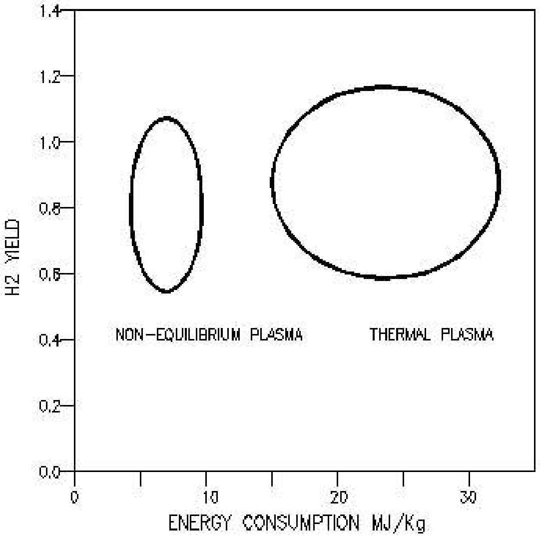
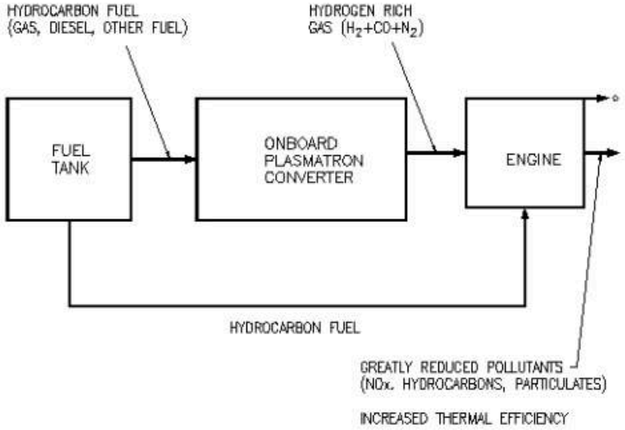


Fig.16.7. The hydrogen conversion efficiencies of equilibrium and no-equilibrium Plasmatron as a function of energy consumption



1608 Fig. 16.8. Emission reduction in an engine using reformed fuel (Figure courtesy of Prof. Daniel Cohn, MIT and SAE International, USA)

17. Shiva's Third Eye

Plasma as the Ultimate Destroyer

Hazardous wastes are legacies of the second wave manufacturing. The intense heat in a plasma jet with temperatures exceeding 5000° C can destroy even the most recalcitrant waste. Waste can be gasified using pyrolysis or sequestered in glass-like medium through vitrification. Many companies all over the world have started manufacturing plasma assisted waste treatment systems. This chapter discusses the properties of plasma sources relevant to waste treatment and describes many commercialised processes.

The Hazardous Waste Problem

Growing populations and affluent societies drive the growth of manufacturing. Consumption of natural resources has accelerated the over the past few decades with concurrent increase in waste generation. Heavy industries like chemicals, petrochemicals, pharmaceuticals and metals recovery and processing produce significant quantities of organic and metal-containing wastes. Recalcitrant wastes such as pesticides, petroleum derivatives, PCBs and other highly chlorinated wastes are of particular concern. Stockpiles of, toxic and bio-accumulative organic pollutants are estimated to include more than one million tonnes of PCBs distributed globally and more than 100,000 tonnes of obsolete pesticides. Chemical weapons form another class of toxic materials, which must be destroyed. This is placing enormous stress on the delicate ecosystems that support life on earth. The pressure on environment is further going to increase because the newly industrialised nations are demanding their place under the sun. Sustainable development with co-existence between nature and the world's industries, economies and lifestyles requires long-term global perspectives, together with more efficient technologies and systems for production, resource conservation and waste minimisation.

India's rapid economic, population and industrial growth over the last four decades has caused severe environmental degradation and pollution problems. Water and land resources have been contaminated by the indiscriminate disposal of residues generated during the treatment of effluents and emissions produced by these industries. India's hazardous waste management market is projected to be $ 200 million in 1999; it is expected to grow by 25 per cent yearly over the next three years. The impetus for environmental remediation and protection is based on "Hazardous Waste (Management and Handling) Rules" that were promulgated by the Ministry of Environment and Forest in 1989. The classification of wastes is being revised to be more consistent with the classification adopted by elsewhere, which considers all categories of wastes: solid, liquid, and gaseous. Because India only recognizes solid and semi-solid wastes as hazardous, the five million tons of wastes that are recognized annually appear minuscule when compared to the 275 million tons of all wastes that are recognized each year by the U.S.

Plasma Pyrolysis

Pyrolysis is the thermal disintegration of carbonaceous material into fragments of compounds in an Oxygen-starved environment. Gasification is a variant of pyrolysis obtained under conditions of partial oxidation. Plasma pyrolysis exploits the thermo chemical properties of plasma in converting solids to gases. The particle kinetic energy in the form of heat is used for decomposing chemicals. In addition, the presence of charged and excited species renders the plasma environment highly reactive which can catalyses homogeneous and heterogeneous chemical reactions. When the process is optimised, the most likely compounds that are to form from carbonaceous matter are Methane, carbon monoxide, Hydrogen, carbon dioxide and water molecules. The high temperature and high enthalpy inhibits the formation of hydrocarbons. Since the plasma process has the option of selecting the gas medium, it helps in changing the by-products. High temperature reduces the required residence time for pyrolysis [Counts 1999].

With carbonaceous wastes such as municipal solid waste, the product gas after pyrolysis is predominantly CO, H_2, HCl and H_2O together with small amounts of fine Carbon. When this mixture which has initial temperature about 5000 K is allowed to slowly cool, below 800°C, back reactions are likely to occur to form dioxins and furans. The chemical composition is frozen at the end of the pyrolysis by rapid quenching to below 100°C, which avoids the formation of these compounds.

The product gas from pyrolysis can be combusted very efficiently producing carbon dioxide, Nitrogen and water vapour as gaseous exhaust to the atmosphere. The slag is a homogeneous, silicometallic monolith with leachate toxicity levels orders of magnitude lower than those of current landfill regulations. The extremely tight physical and chemical bonds within the slag result in consistently low leachate characteristics.

Typical waste stream compositions may be dominant in organics, inorganics, soil, concrete, or concentrates of specific compounds. The hazardous compounds are usually in small or trace amounts. The plasma process destroys or alters the hazardous characteristics or chemistry of the waste compounds. Toxic metals can be incorporated in the solid solution or volatilised, and collected in the off gas treatment system for concentration and resale or stabilisation and disposal. Examples of potential by-products are liquid methanol fuel, fuel gas for heating or absorption air conditioning, carbon black, concentrated "metal ores", construction aggregate, and paving or decorative bricks. The process also reduces stack emissions to below present limits by reducing total exhaust gas, as well as by using improved off-gas collection methods.

Plasma Vitrification

An alternative to pyrolysis for waste destruction is vitrification. Plasma torches are replacing combustion burners and electrical heaters for in-situ remediation of contaminated soils [Mitchell 1981]. In this approach, the heat source enclosed in a casing is lowered into the treatment zone. Plasma melts nearby material to create a dense, molten mass at the bottom of an expanding cavity. As the heat source is slowly withdrawn, additional material glides off the walls and mixes with molten material below, creating a column of vitrified matter that solidifies as it cools. Off-gases from the melt zone are withdrawn through the annulus between the casing and the electrode for cleanup and release. High operating temperatures and the ability to add oxidants and glass-formers enable plasma technologies to work in high-silica soil and other hard-to-treat materials.

Vitrification has many advantages from the waste treatment point of view. It can simultaneously process varieties of waste, like organic, inorganic or radioactive [Johnson 2002]. It can be applied for in-situ as well as ex-situ situations. Since it is an air-free process, the off-gas requiring additional treatment is minimised. Vitrification is independent of the fuel value of the material being processed.

Plasma Sources for Waste Treatment

The plasma arc using Carbon electrodes was first used in the 1960s as a source of intense heat. However, the short lifetime of the electrodes was a major impediment in the successful development of this technology. With dramatic developments in plasma sources, plasma technology is now applied to highly toxic and refractory compounds and the final products can be harmless gases. For example, the abundant ultraviolet radiation in thermal plasma can dehydrogenate organic Chlorine. The reactors can process gaseous, liquid and solid materials.

The workhorse of plasma based waste destruction is the plasma torch. Plasma torches are electrical discharge plasma sources with the plasma being extracted as a jet through an opening in the electrode and out of the confines of the cathode-anode space. The inherent thermal and electromagnetic instabilities of the arc column are stabilised by forced gas flow along the current path or by interaction with a guiding wall or by external magnetic fields.

The driver for the development of plasma torches was the space race in the 1960's. Missiles re-entering the atmosphere create shock-ionised air plasma. Laboratory simulation of these conditions was necessary for the development of materials capable of withstanding the searing heat of the re-entry plasma. Subsequently, arc systems were designed to generate the re-entry conditions using clean, high enthalpy gases at high stagnation pressures. Many of the present day plasma torches are derivatives of the plasma jet sources built for this application. A typical plasma torch in operation is shown in fig. 17.1. A plasma torch produces plasmas by sending electrical currents at high voltages through an initially nonconducting high-speed gas flow. Plasma temperatures can easily reach tens of thousands of degrees and high enthalpy gas flows can be generated in large reaction volumes.

DC arc, RF and microwave plasma sources can be converted into plasma torches. However the commercial plasma sources are based on direct or alternating current arcs. The high speed gas flow in the torch aids in effective heat transfer and effective insulation of the electrodes from the arc heat. The energy density in the arc jet can be as high as 10^9-10^{10} Wm^{-2} [Rutberg 2003]. Three phase AC arc sources utilise the fact that at current zero in one phase, the arc gets transferred to another pair of active electrodes. Plasma torches upto 3 MW power capacity has been built by Westinghouse and the Institute of Problems of Electrophysics in Russia [Glebov 1985]

Although a large number of plasma torches are available commercially, their fundamental design can be traced to a few generic concepts [Camacho 1988]. A schematic representation of these concepts is given in Figure 17.2a-d. The Huls torch is perhaps the earliest industrial plasma torch developed in 1925 at Chemische Werkes Huls for acetelyn manufacturing. It is a nontransferred torch using water-cooled hollow Copper and Steel electrodes of different diameters. Gas is tangentially injected into the arc to minimise the erosion of the electrodes and to stabilize the arc.

The Linde division of Union Carbide Corporation developed air heater torches in 1960 and supplied them to NASA with power ranging from 2-20 MW. It is a non-transferred design with two hollow alloy Copper electrodes of equal diameter. The cathode attachment is rotated using an axial magnetic field to interact with the radial arc root and to generate an azimuthal force. The Westinghouse torch is similar to the Huls design except for the axial magnetic field, which is applied to both cathode and anode regions. Amongst the transferred arc torches we must mention the Voest-Alpine torch based on the design developed at the Paton Institute at Kiev and transferred to Edelstrahlwerke at Freital in the former East Germany. This uses a solid Tungsten electrode recessed behind a Copper nozzle. A commercially successful design of a segmented plasma torch manufactured by ScanArc Plasma Technologies is schematically shown in Fig. 17.3. The engineering details of such a system is given in Fig. 17.4

The basic characteristics of plasma as a tool for pyrolysis are high operating temperature, high chemical reactivity, low gas flow rates, controlled processing atmosphere and rapid system response. Generation of heat in the plasma torch is through the Ohmic dissipation of electrical energy in the gas and is independent of the chemistry involved. This results in high temperatures in both combustible and non-combustible materials. The plasma environment can be chosen to be oxidising, reducing or inert, giving independent control of the chemistry. Plasma systems use relatively small gas quantities, which minimises the requirements for exhaust gas scrubbing. The smaller gas flow also allows treatment of fine dusts without significant carry over into the exhaust gas treatment systems. An arc plasma system operates at high energy densities and temperatures so that compact reactors with high processing rates are possible. The clean, compact systems are generally free from locational constraints imposed by environmental regulations.

Plasma Pyrolysis System

Plasma pyrolysis systems are generally custom-built to meet the large diversity in type, size and quantity of waste material to be processed. The raw waste is introduced into the gasification system by a feeder mechanism specific to the type of material to be processed. The feeder is designed to introduce waste material into the hottest region within the reactor vessel, and to minimise the entry of air, during the charging with waste.

The waste is then processed within a reactor vessel lined with refractory material, which is preheated to a minimum of approximately 1,1OO°C before any processing commences. The reactor vessel operates close to atmospheric pressure. Though the chemical composition of the waste determines the electrical energy required to gasify it, approximately 1 kWh of electrical energy is required to process a kilogram of waste. Plasma arc torches are available in sizes ranging from 50 kW to over 3 MW; therefore, plasma gasification systems can be implemented at virtually any capacity. The very high temperature profile of the plasma provides an optimum processing zone within the reactor vessel through which all input waste material is forced to pass.

The product gas from the reactor vessel passes through the pollution abatement system, which is selected for the processing of the specific type and volume of input waste materials. This off-gas must pass through a secondary combustion chamber to assure complete oxidation of hydrocarbons and destruction of toxic compounds. To achieve destruction and removal efficiency (DRE) of 99.999 per cent or greater for organic substances, the standard design for a secondary chamber keeps the gas at 1000^{o} C in an oxygen rich environment for at least two seconds. Natural gas or oil fired combustion burners are used to provide complete combustion if the pyrolysis product gas has low calorific value. The secondary chamber walls have thick refractory lining to minimise heat loss and protect the steel walls.

A particulate control component removes any particulate matter, which remains in suspension within the product gas, and a wet scrubber system removes organics and acid gases. The wet scrubber uses jets of caustic soda for the scrubbing of acid gases along with any other molecules from the gas stream. The pH of the wet scrubber water is automatically monitored and controlled by a pH control mechanism. A mildly caustic scrubber solution (pH maintained at 8.5) is used in the quench tank, jet scrubber, and packed-bed scrubber. The chilled scrubber water proceeds first to the quench tank, from where it passes to a jet scrubber, which is designed to remove particulates and acid gases. A counter-flow packed bed scrubber provides additional removal of acid gases. A de-mister removes moisture droplets entrained in the flow. The product gas, the torch water cooling and scrubber water subsystems contains substantial sensible heat, which can be recovered.

Molten slag is extracted from the reactor vessel through a tap attached to the reactor vessel. The slag is allowed to accumulate in the bottom of the vessel to a predetermined level dictated by the amount of waste processed. The molten slag can be used for manufacture of rock wool insulation or can be poured directly into moulds and allowed to cool in free air to provide vitrified ingots for direct delivery to off-site clients for reuse.

Mobile plasma gasification systems have been developed to provide waste disposal service to locations, which do not have enough quantities of waste to justify dedicated installation, or to customers with waste streams, which cannot easily be transported due to their hazardous nature.

The consistently low environmental emission characteristics exhibited by plasma gasification indicate that it can be used as a waste treatment alternative to other technologies with substantial improvements in environmental emission level for both air emissions and slag leachate toxicity. Air emission characteristics indicate that current air emission standards are easily achieved and substantially bettered by an operational plasma gasification system with an exhaust flue less than 20 ft high.

Bacteria survival results indicate that not even the most heat resistant spores can survive the process at even the most stringent challenge population. Destruction removal efficiency (DRE) results in excess of seven nines have been consistently achieved with highly chlorinated industrial hazardous waste materials.

Instruments for characterising and monitoring the chemical nature of the waste as are under development. One focus is development of optical sensors for the remote monitoring of mixed radioactive and organic wastes in soils. Analysis of the toxicity of the waste and potential health hazard is another area. Modelling the plasma dynamics and chemistry within the chamber is another challenging area. The environment within the chamber is primarily defined by several temperature measurements. Two-colour pyrometry is used to determine the molten slag temperature and a suite of thermocouples within the chamber indicate a slighter cooler gas phase temperature. Synthetic spectra are generated from radiation transport calculations and compared with optical emission spectroscopy to map the gas temperature around the plasma arc itself. Spectroscopy offers the potential of a non-invasive diagnostic eventually to be used for on-line process control, a necessary feature for an operating system due to the heterogeneous waste stream.

Persistent Organic Pollutants

PCBs are chemical substances, which accumulate in biological systems, and pose a risk of causing adverse effects to human health and the environment [UNEP 1999]. They can be transported long distances, and have been detected in the farthest corners of the globe. While manufacture of PCBs has reportedly ceased, the potential or actual release of PCBs into the environment has not, since significant quantities of existing PCBs continue in use or in storage.

Recognising that PCBs once released into the environment could pose a threat for decades to come, UNEP included PCBs among the 12 persistent organic pollutants (POPs) identified for international action. The Council concluded that international action, including a legally binding global instrument, is required to reduce the risks to human health and the environment arising from the release of the 12 POPs (PCBs, dioxins and furans, aldrin, dieldrin, DDT, endrin, chlordane, hexachlorobenzene, mirex, toxaphene, and heptachlor). The Council also requested UNEP to initiate a number of immediate actions, including intensifying POPs information exchange; improving the availability of information on alternatives to POPs; developing an inventory of PCB destruction capacities and assisting countries in identifying PCBs; and assisting countries n identifying dioxin and furan sources.

The commercial manufacturing of PCBs started around 1930 for use as liquid insulator for application in electrical equipment such as capacitors and transformers. By the time they were phased out in mid-1980s, a few million tonnes were already manufactured. A series of international agreements culminating in the Basel Convention now govern the transboundary movement and disposal [UNEP 1998] of PCBs.

The destruction of PCB requires the breaking of molecular bonds by an input of chemical or thermal energy. The quality of destruction is characterised by a Destruction Removal Efficiency (DRE) given by:

DRE = $W_{in} - W_{out}/W_{in}$ where W_{in} is the mass feed rate and W_{out} is the mass emission rate. The destruction cost ranges from $ 200 to $ 1000 per tonne.

The common destruction technology for PCB as well as the PCB-contaminated materials is incineration. Incomplete combustion of PCBs and a low speed of effluent gas cooling in the critical temperature range of 200-400° C can generate significant levels of dioxins. Dioxins are more toxic than the PCBs and are generally formed when partially degraded organic fragments recombine [UNEP 2000].

The high temperature of the plasma torch ensures functional destruction of PCB by reducing complex molecules into simpler ones (CH_4, HCl, H_2, N_2). Good level of turbulence and residence time (at least 2 s) ensures a very good burning efficiency (at least DRE=99.9999 per cent). Plasma pyrolysis avoids formation of dioxins by using high quench rate of secondary products and performing the destruction in an environment devoid of oxygen.

The Medical Waste Problem

An international scandal involving a vast intra-European traffic in medical waste originating from Germany and culminating in eventual redistribution in other European markets shocked the world into recognising the magnitude of the medical waste disposal problem [Rogers 1992]. India is no stranger to such horror stories. Recycled syringes and quilts packed with used surgical cotton have a thriving market. In 1991 Pioneer reported a well-knit racket operating from the backyards of the All India Institute of Medial Sciences in Delhi, which transported contaminated syringes to Meerut [Down to Earth 1996].

Pathogens of deadly diseases like hepatitis B find fertile breeding ground in the piles of undisposed medical waste. Medical waste requires special handling, treatment, and disposal, usually according to specific regulations and guidelines. Such waste may pose potential health, safety, or environmental hazards. These wastes are usually collected, stored, and disposed of separately. Though medical waste comprises of all the waste generated in health care establishments including hospitals and research laboratories, 75 to 90 per cent of such waste originates in the house keeping functions and is innocuous. The remaining 10-25 per cent consists of chemical waste, infectious waste, and radioactive waste and is considered hazardous and requires special treatment. Infectious waste is known as red bag waste and includes materials considered to be potential health hazards because of possible contamination with pathogenic micro organisms, infected animal carcasses, organic tissues and body parts. Typical medical waste components are shown in Table 17.1.

Historically, land filling was the most preferred means of disposal of medical waste. Public opposition and positive correlation with ground water contamination have resulted in this option steadily going out of favour. In many countries, medical waste can no longer be disposed in landfills unless it is so thoroughly disinfected as to pose no risk to human health.

Incineration or burning of waste material in open air can never be complete, with small quantities of many organic and chlorinated organic compounds as well as pathogens surviving. This will lead to dispersal of dangerous pathogens. Incineration is currently used to destroy hospital waste especially biomedical waste and hazardous chemical waste by reducing volume and destroying some harmful constituents. Airflow that is in excess of the stoichiometric requirement for combustion is essential for incinerator to enhance the combustion process. The demand for excess airflow limits the temperature that is required for incineration. Due to insufficient temperature generated in the process chamber, incinerators produce extremely toxic products. This can cause air pollution or the toxic pollutants can remain at the bottom ash, eventually finding its way into landfill. Of particular concern is the formation of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (often referred to as dioxins and furans), which are extremely toxic and persistent in the environment. Dioxins and furans are formed as a result of reaction during the cooling of the stack gases.

Microwave disinfection achieves sterilization by subjecting medical waste to shredding, high temperature steam injection and microwaves. The treated end product is suitable for landfill or waste to energy plants. Systems are available which can process from 200 to 900 pounds per hour. The equipment is unable to process radioactive, chemically hazardous or gross anatomical waste. The major drawback with microwave system is, small reduction in volume and possibility of infection if the shredding is not automatic.

Infrared sterilization uses infrared rays with resistance or convection heating to sterilize medical waste. This technology can be used for a variety of types of medical waste including microbiology waste and human blood products. It achieves a waste reduction of 90 per cent and sterilized waste can be disposed of in landfills. The market for infrared sterilization technology includes smaller health care facilities such as clinics, laboratories, nursing homes, blood banks and small hospitals.

Electro-pyrolysis oxidation (Bio-Oxidizer) uses pyrolysis and oxidation to treat bio-hazardous waste. Red bag, pathological and general hospital waste can be processed, achieving reductions of up to 95 per cent in mass and volume. The process eliminates air emissions and produces ash, which is non-hazardous and can be disposed of in local landfills. The market for electro-pyrolysis oxidation technology includes medium to large hospitals and health care facilities.

In plasma pyrolysis, the high temperature and high enthalpy inhibits the formation of hydrocarbons [Camacho 1991]. Plasma process has option of selecting the gas medium, which helps in changing the by-products. High temperature yields more amounts of gaseous by-products and reduces the required residence time for pyrolysis and for disinfecting the waste.

The first medical waste pyrolysis system was established at the Lyon Medical centre in France in 1991. The collaborators of the Plasmapole project were Aerospatiale, EdF, Group Lyonnaise and Streichenberger Energies Services. The 1.3 MW plasma torch is capable of destroying 10,000 MT of waste annually. The specific energy requirement reported by Aerospatiale is in the range of 900 kWh/ton for a 600 kW system. The highly sticky greasy ash left by the conventional incineration process is not observed in plasma treatment.

The recent trend is to build small sized treatment systems [Fig. 17.5 and 17.6] for use in medium size hospital [Nema 2002]. The system is compact and has a footprint of 2.5 metres by 1.5 metre. The waste is introduced into the pyrolysis chamber through a load lock valve designed to allow waste charging without air entry during the pyrolysis process. An inexpensive graphite electrode torch with consumable anode is used to treat the waste. The pyrolysed gases are burned in the combustion chamber reaching the statutory 1100 degree temperature and specially designed baffles keep the residence time at 2 seconds. The emission characteristics of this system are given in table 17.2.

Chemical Weapons

Plasma pyrolysis has been developed for the destruction of a variety of waste materials including chemical warfare agents in the PLASMOX® process. A plant is being constructed at Munster, Germany to address the disposal of viscous or solid chemical agents and, in particular, arsenic's as well as for the clean up of arsenic contaminated soil [Pearson 2002].

The process involves a soil washing and flotation stage to separate contaminants from the soil. These contaminants and any arsenical chemical agents are then destroyed by thermal destruction and vitrification using the PLASMOX process to heat the feed material to temperatures of 1400 to 1600 °C in a plasma high-temperature reactor, which is a cylindrical chamber with a centrifuge at the bottom rotating at about 40 revolutions per minute into which is introduced the feed material. The plasma torches cause the rotating feed material to pyrolyse. The capacity of the centrifuge is about 1 m^3, which holds about 2 to 5 tonnes of smelt depending on its density. After 4 h, the centrifuge is stopped and the melted material is discharged into a slag cart. The quality of the smelt and of the solidified slag, respectively, can be influenced by the use of additives. In the PLASMOX process in Germany, the arsenicals are largely transferred into the gas phase because of the high temperatures and are precipitated in the PAS scrubbers as iron arsenates. This sludge is dried and put into drums for underground storage. Other heavy metals remain in the slag, which is similar to glass where they are evenly distributed and firmly bound. The EPA standard leach test in which the slag is treated in a slightly acidic environment to simulate the effect over time of acid rain on the dumped material resulted in the various elements in the slag being released in only extremely small quantities into the leach test eluate. As an inert substance, this material can be used as a filling material in civil engineering and is not required to go to a hazardous waste landfill site.

Nuclear Waste

Radioactive waste from nuclear power plants is considered very hazardous because of the fact that exposure to human beings can cause cancer. The radiotoxicity depends on a variety of factors like physical half-life, biological half-life, sensitivity of the organ or tissue where the nuclide is likely to concentrate, ionizing power of the radiation from the nuclide that depends on the energy of the radiation emitted from the radionuclide, etc. Based on these, radioactive nuclides of elements like 137Cs or 90Sr or 131I are considered to be the most hazardous on the scale of the human lifetime. Other long-life nuclides like 239Pu, 241Am, and 237Np pose a long-term hazard, on the other hand, to future generations [Rao 2001]

Waste consisting of the spent fuel, effluents arising from the reprocessing of spent fuel and the solids into which the liquid waste is converted is categorised as high-level radioactive waste. The radioactive fission fragments decay to different innocuous stable elements via different nuclear reaction routes in about 1000 years. On the other hand, transuranics take nearly 500,000 years to reach such levels. Most of the radioactive isotopes in high-level waste emit large amounts of radiation. They have extremely long half-lives (some longer than 100,000 years), demanding long time-periods before the waste will settle to safe levels of radioactivity. Large amounts of waste contaminated with small amounts of radionuclides, such as contaminated equipment (glove boxes, air filters, shielding materials and laboratory equipment) protective clothing, cleaning rags, etc. constitute low-level radioactive waste. Even components of decommissioned reactors may come under this category after being subjected to part decontamination procedures. The level of radioactivity and half-lives of radioactive isotopes in low-level waste are relatively small. Storing the waste for a period of 10 to 50 years will allow most of the radioactive isotopes in low-level waste to decay, at which point the waste can be disposed of as normal refuse.

Safe disposal of the nuclear wastes is a vexing environmental issue. Nuclear waste is generally treated by trapping high-level nuclear wastes (HLW) in borosilicate glass and stored in a controlled repository. Spent fuels are generally reprocessed. Some low-level nuclear wastes (LLW) are incinerated with the ash temporarily stabilised and deposited in a regulated, near surface repository. For some LLW and intermediate-level nuclear wastes, which include transuranic-contaminated wastes and decommissioned nuclear plants the appropriate treatment methods are still being determined. The major issues include safety during treatment, appropriate final waste composition and structure, minimisation of the final waste volume, and stability requirements of the repositories for different radioactive waste forms.

High concentrations and long-lived radionuclides can be stabilised in glass or ceramics. The waste loading may vary depending on the glass/ceramic selected. For intermediate-level wastes, BSG has a waste loading of 20-30 per cent while basalt-like glass/ceramics have residue waste loading of 40-100 per cent. Similar waste loading is found for LLW and NPW; therefore, a basalt-like glass-ceramic waste form will give the maximum volume reduction for LLW and NPW.

The plasma arc melts inorganics and metals into molten glass or metal and tapped into storage canisters. The organics are paralysed and oxidised. Halides and sulphur compounds are vaporised and collected in the off gas collection system, as are any volatilised metals. The melter is operated with a low temperature cold top of waste feed material that inhibits volatilisation. After quench and scrubber sections, prefilters, activated carbon filters, and HEPA filters are employed as required to meet environmental regulations. Special treatment is required for some mixed waste containing relatively high concentrations of Mercury, Tritium, and C-14.

The overall volume reduction can be greater than 100:1. Almost all of the short-lived and long-lived radionuclides are stabilised in a long-lived final rock form that has geological analogues that have lasted millions of years. The few radionuclides that are volatilised or entrained into the off gas are collected in a small-volume secondary waste form that qualifies as LLW and near surface disposal. The secondary waste form could be glass, sol gel, or possibly cement, depending on the composition and activity level. High metal concentrations in the waste can be separated out and recycled for shielding, for containers, or for increased volume reduction in disposal. These metals will be decontaminated to a great extent by the slag/metal reactions. Contaminated filters and other process wastes can be fed into the melter.

The plasma arc melter systems used for treating radioactive wastes are relatively small, compared to those for industrial or municipal wastes. Economies of scale can still be accomplished with larger units. Recent demonstrations have shown costs of approximately $13,000/tonne. A specific system which has been discussed in the literature is the Plasma Hearth Process (PHP) built and operated at the Argonne National Laboratory since 1996 [McFarlane 1997]. PHP is designed to treat closed 208-litre containers thereby reducing handling requirements, costs, secondary wastes, and worker exposures.

Nuclear waste treatment has to meet very stringent environmental regulations imposed by the Environmental Protection Agency (EPA). Resistance to groundwater leaching is evaluated by the Toxicity Characteristic Leaching Procedure [EPA 1986] in which the waste is immersed in water, and the concentrations of particular hazardous materials in the leachate is measured. Long-term durability determinations typically include the Product Consistency Test, which is similar to the TCLP but exploits a longer exposure to characterise the waste form.

Radioactive waste treatment systems must ensure that secondary waste is not generated in the destruction process. Some material especially high-vapour pressure hazardous metals can be oxidized and migrate to the slag. Radionuclides can permeate into the off-gas stream, which creates a new mixed-waste stream that requires further treatment. Off-gas measurements [Carney 1996] generally deployed include in-situ and extractive Fourier transform interferometry measurements for volatile organic vapours; laser-induced breakdown spectroscopy measurements for metal vapours etc.

Soil Vitrification

Permanent structural changes in the clay occur at temperatures above 500° C, [Hausmann 1990] and the clay minerals start melting in the temperature range of 1100-1600° C [Dragun 1991]. The magma state represents substantial volume reduction as individual particles fuse and melt. The rapid cooling of the molten material produces a predominantly glassy object. Formation of an amorphous rock is thermodynamically favoured since the cooling is rapid enough preventing crystal formation. The final products include a glassy rock similar to obsidian and porous basalt. The durability of this material has been verified by the Soxhlet corrosion rate, and has been found to be comparable to that of Pyrex glassware [Buelt 1987]. The in-situ vitrification of contaminated soils involves the complete meltdown of clay, silt, or sand at very high temperatures, typically 7000 degrees C thereby forming magma, which subsequently cools into two types of igneous rock..

The torch is lowered into a steel chamber filled with clay or sand. The plasma flame creates a pool of molten material. After 40 hours of cooling, it is excavated to uncover a spheroidal core of non-porous glassy rock. Applications of the method include in-situ modification of unstable foundation soils, buried wastes, and radioactive and other contaminated ground. Geo-environmental remediation is also possible, especially since the plasma process works under water.

1-MW Plasma torch developed by Plasma Technology Corporation has been tested in full-scale melts in the Savannah River Site in 1996. Three melts in uncontaminated SRS soil produced vitrified columns 2–3.5 feet in diameter and weighing 600–1,100 pounds. Funded in part by DOE, developers are working to prolong electrode life and improve the integrity of the cooling system in a project planned to culminate in field-scale demonstrations.

The plasma arc between a hollow, outer graphite cylinder and a central graphite rod projects a 2,000–3,000ºC plume of hot plasma. The robust graphite electrodes do not require cooling, so a high portion of the expended power goes into the melting process. Using a 500-kW power source in its laboratory, Montec has performed over 30 pilot-scale melts in uncontaminated soils of various compositions and moisture content, yielding monoliths up to a meter in diameter and weighing over a ton. Montec is teaming with Oak Ridge National Laboratory to demonstrate remediation of mixed buried wastes deemed difficult for conventional ISV, such as volatile materials and containers of liquids.

Treatment of Incinerator Ashes

In the developed world, a large and increasing proportion of combustible solid waste is incinerated in order to reduce their mass and volume to lower landfill costs and also generate electrical power to offset treatment costs. Over 100 million tonnes of municipal solid waste (MSW) and 4 million tonnes of sewage sludge waste (SSW) are burned annually worldwide. The ashes produced from incineration (around 15-20 per cent by mass of the feed material), are of low bulk density and contain leachable toxic heavy metal species and persistent organics. At present, the majority of incinerator ashes are land filled. However, in many countries, this situation is liable to change, as suitable landfill sites become increasingly scarce and the laws regulating waste dumping become more stringent. DC plasma furnace for the vitrification of waste ashes generated in the incineration MSW and SSW has been developed by Tetronics at demonstration and pilot plant scale, with feed rates of 50 kg /h or 350 kg/ h respectively and at commercial scale at up to 30 T/day. The vitrified final product from both operations easily meets the legislative limits regarding landfill disposal. Furthermore, the product can be utilized in a number of building and other material applications thereby further enhancing the process economics.

The twin DC plasma arc heating system was designed to have a high degree of flexibility allowing the use of either hollow graphite electrodes or water-cooled plasma torches. The furnace was water cooled and lined with high grade alumina refractory. During operation the furnace was purged with argon to prevent air ingress. Ash feeding follows a 2-3 hour furnace preheat schedule. The plasma power to feed ratio is adjusted to ensure efficient melting and assimilation of the feed.

The exhaust gases are analyzed for CO, CO_2, H_2, H_2O, HCl, HF, SO_x, NO_x and persistent organics. At the completion of a run, typically after 30-40 kg material is consumed, the feed and power to the reactor are switched off and the treated material allowed to cool, prior to removal. Both the residual feed and the product weights are recorded for mass balance purposes. Representative samples of both the fused product (which sometimes included free metal) and the fume are taken for analysis.

For the MSW and SSW grate ashes around 92-95 wt per centage of the ash feed are converted to slag. In the case of MSW fly ash, slag yields in the region of 80 wt per centage were achieved. This lower recovery rate is largely due to the high content of chloride, sulphate and other volatiles present in the feed. All leachates from the slags fall below legislation concentrations. By contrast, the MSW fly ash failed to meet the TCLP standards with respect to Cd and Pb. Furthermore, the MSW grate ash also exceeded the allowable lead limit and the SSW ash leachate was high in arsenic. The toxic equivalent (TE) concentration of dioxins and furans in the initial MSW fly ash was 5-10 ng/gm, which was reduced to 0.002 ng/gm in the secondary fume from the plasma reactor.

A number of pilot plant ash treatment systems incorporating Tetronics plasma technology has been successfully commissioned. All these facilities have been demonstrated to be robust, simple to operate and produce an environmentally stable slag. As a result of these successful pilot scale operations, the installation of a 30 tonne/day commercial scale DC plasma arc ash melting system is to be undertaken in the near future.

International Status

Plasma pyrolysis technology has been used widely for the safe disposal of toxic and hazardous. Various companies have demonstrated the pyrolysis of different waste using thermal plasma technology. The following is a review of advertised processes, gathered mainly from company hand-outs and websites. Peer reviewed literature is apparently quite scarce in this field. Plasma based processes are generally treated as dual-use technology and there is a general reluctance to share information, with a few notable exceptions.

Plascon is an in-flight plasma arc system developed by Australia's CSIRO for treating liquid or gaseous waste stream, which is injected directly into a plasma flame [Ramakrishnan 1993]. The residence time of the waste in the reaction chamber is of the order of 20-50 milliseconds, resulting in a small process inventory. The end products include gases consisting of argon, carbon dioxide and water vapour and an aqueous solution of inorganic sodium salts. Chlorinated organics yield very high destruction performance and release very low dioxins and furans. The measured emission of dioxins and furans in the off gases has been found to be in the range of 0.005 - 0.009 ng/m^3, which is well below the strictest proposed environmental standard in the world.

MeltTran system exploits 200 kW graphite arc melters for treating landfills and high organic content wastes. Small systems required mainly for the destruction or alteration of the hazardous nature of the waste can be built at lower capital costs.

Plasma Environmental Technologies Inc (PEAT) has developed many processes for waste treatment. PARCON was developed specifically for destruction of problematic liquid chemical wastes, including pesticides, PCBs, chemical weapons, fungicides, and petroleum derivatives. Destruction and Removal Efficiency exceeds the EPA standard of 99.9999 per cent, with documented DRE as high as > 99.999998 per cent. For example, the PARCON emission of dioxin/furan has been documented at 0.03 nanograms per cubic metre (ng/Nm^3), against the US-EPA allowed level of 0.2 ng/Nm^3. PARCON technology is available in transportable units ranging from 12.5 kilograms per hour to > 200 kg/hour feed capacity. The furnace uses a transferred arc plasma torch to heat the bath material. PEAT was involved in the medical waste treatment project at Kaiser Permanente Hospital in San Diego, which was abandoned before completion.

Retech Systems LLC is a division of Lockheed Martin Environmental Systems and Technology. The Plasma Arc Centrifugal Treatment (PACT) process was developed by. The waste is fed continuously into the centrifugal reactor by a screw feeder. Solid material is retained in the tub by centrifugal force. The destruction and removal efficiency (DRE) of organic compounds is claimed to be greater than 99.99 per cent. The system can operate under pyrolytic conditions and a reducing atmosphere avoiding dioxin formation in the primary chamber. Investment costs are located in the range 3.8-7.6 millions of ECU while the operating costs may be evaluated around 120-150 ECU/ton.

Rhone-Poulene, with the collaboration of EdF, Aerospatiale and Spie Batignolles have built a rotating furnace for the destruction of industrial chemical waste at their Pont de Claix site. The plant is rated at 800 kW and has been designed to accept 200 kg packed drums [Cretenot 1990]. They intend to use it for the destruction of highly chlorinated wastes generated in their own chemical facilities.

The Startech Environmental Corporation developed the STARTECH Plasma-electric Waste Converter (PWC) operating in an oxygen deficient or reducing atmosphere. Organic and inorganic wastes can be introduced into the plasma chamber as solids, liquids, gases, and sludge. Gas recovered from the top of the chamber is treated and can be reused as fuel gas or chemical feed stock to produce, for example, polymers.

Aerospatiale, the French company developed the INCIDIS process to demonstrate the efficiency of plasma treatment in disposing of solids holding high percentage of chlorinate compounds such as PCBs. The torch used has a power rating of 800 kW and waste held in bins are reduced in a liquid mixture and pumped in contact with plasma flame, which destroys harmful molecules and produces neutral slag. Trials carried out with pentaclorophenol showed a DRE > 99.999 per cent and a VOC (volatile organic compounds) < 2.6 mg/Nm^3. The total cost of disposal is fixed around 450 ECU/ton.

Westinghouse Plasma Corporation has been in plasma-based applications since 1950. In 1986 they developed a mobile plasma plant for disposal of liquid organic material such as PCBs. The plasma plant was based on a 1MW non-transferred plasma torch. This plant demonstrated good results for the disposal of methanol, ethanol, methyl ethylketone, and carbon tetrachloride. The most interesting results arise from PCBs incineration in fact, with a torch power supply of 850 kW, a destruction efficiency (DRE) beyond 99.99999 per cent had been reached with emissions of HCl, particulate and NOx which were below the accepted regulatory guidelines. Furthermore dioxins and furans emissions were usually undetectable.

Pyrolysis System Inc. has developed mobile pilot-scale plasma system for the destruction of liquid Hazardous waste such as PCBs. The system is basically composed by a plasma torch able to reach the typical temperature of 10000 C°, a reactor where the reaction takes place, a scrubber system and a gas effluent system; emissions had been measured by a monitoring system. In 1985, trials for PCB destruction have been carried out by highlighting DRE efficiency beyond 99.9999 per cent and HCl formation rate below 4 kg/hr. In the scrubber effluents and in the exhausted gases as well, an appreciable concentration of dioxins or furans has not been noticed.

PLASMARC plant built by MGC Plasma AG in collaboration with Technip Germany is a closed reactor vessel equipped with a transferred plasma torch and an oxygen-fuel lance. The torch power is rated upto 1.2 MW. Though designed for general-purpose waste treatment, they have demonstrated treatment of nuclear waste also in this system. The oxygen-fuel is added to heat up the system and to keep the reactor on required temperature during treatment of low caloric material. Within Plasma reactor the amount of dust in the off-gas is normally low.

The PYROARC process has been tested in the pilot plant built by ScanArc Plasma Technologies, Sweden, since 1986. The test furnace has a capacity of 300-700 kg of solid wastes per hour, depending on waste composition, and a capacity of 50-500 kg of liquid or gaseous waste per hour. The plant is equipped for continuous operation up to four days. Dry or wet gas cleaning systems can be used.

Waste materials tested so far with good results are: refuse derived fuel, spent tyres, hospital waste, chlorinated solvents, PCB oils etc. The process is claimed to meet the most stringent environmental demands while the amount of secondary products, which has to be disposed of, is kept to a minimum. A novel approach, in contrast with most manufacturers is to build smaller plants to serve local areas than big centralised plants.

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Table 1: Typical Hospital Waste Constituents

Waste	**Weight (%)**
Paper & Cloth items	50-70%
Plastic	20-60%
Glassware	10-20%
Fluids	1-10%

Table II: Emission data for Medical Waste Pyrolysis System

Gas	CPCB* limit ppm	Measured ppm**
CO	100	40-85
NOx	450	7-25
SOx	50	1-20
Hydrocarbons	100	10-95
HCl	50	--

- CPCB = Central Pollution Control Board, the statutory environmental regulation body in India
- ** Gas emission data is instantaneous. Averaging usually done reduces these values further.

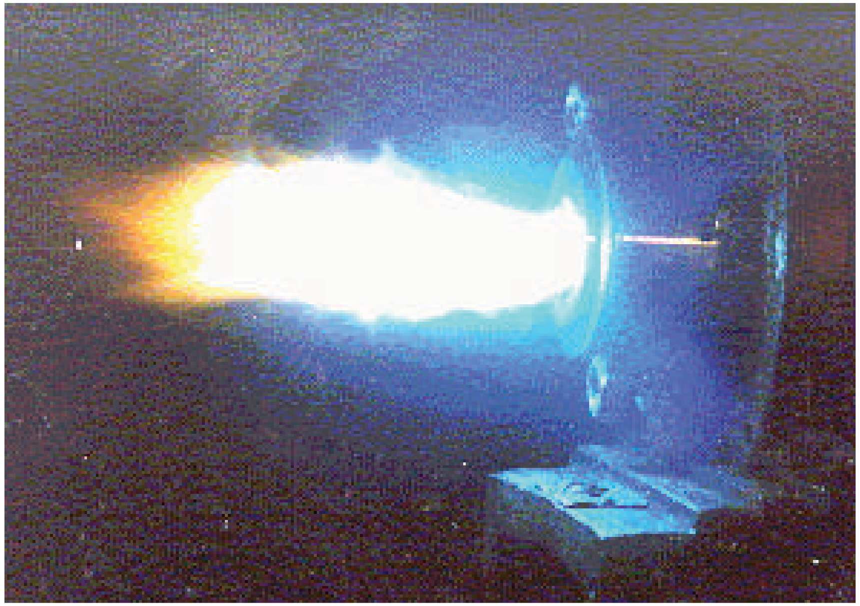

Fig. 17.1. Photograph of a high power plasma torch in operation

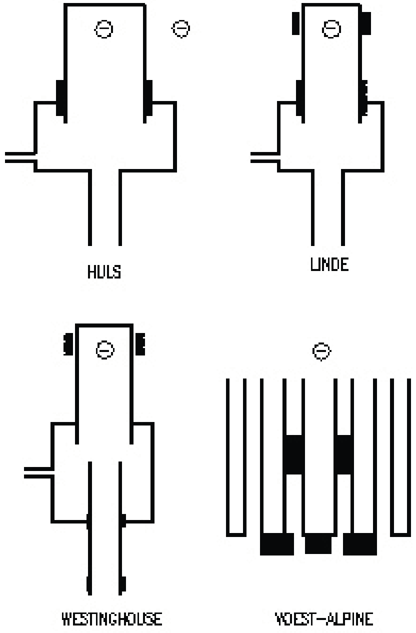

Fig. 17.2. Schematic diagram of generic plasma torches

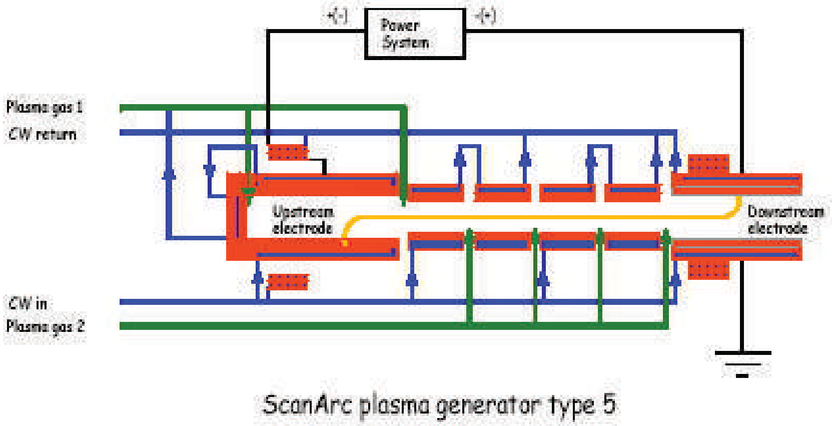

Fig. 17.3. Schematic diagram of a segmented plasma torch (Figure courtesy of ScanArc Plasma Technologies)

Fig. 17.4. Photograph showing the engineering details of a high power commercial plasma torch (Photo courtesy of ScanArc Plasma Technologies)

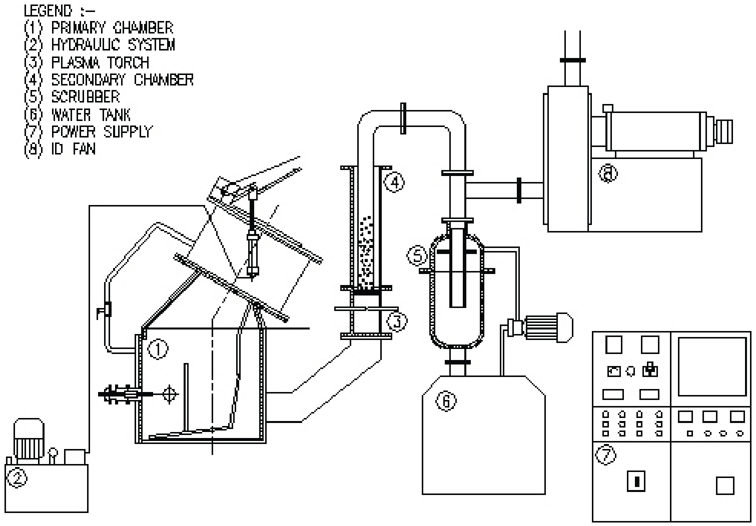

Fig. 17.5. Functional diagram of a medical waste pyrolysis system

Fig. 17.6. Compact medical waste pyrolysis system built in India (Photo courtesy BPS, Ahmedabad)

18. Greening of the Foundry

Plasma Mediated Metallurgy

Metallurgy is one of the oldest technologies. It also has a very high pollution potential because of the use of complex ores, hydrocarbon heating sources and the resultant emissions. Plasma techniques are invading this field to improve its efficiency, to enable it to use cheaper raw materials and to reduce the environmental impact. This chapter will review major developments in plasma-mediated metallurgy.

Plasma as a Metallurgical Processing Tool

Metallurgy including large-scale steel making is on the crossroads. Considerations of economy and environmental impact are generating needs for improved and efficient processes, reduction of raw materials and energy and cleaning up the process. The ecological cost of conventional metallurgy is assessed to be 25 per cent of the product cost [Tsvetkov 1999]. Techniques like direct reduction where the synthesis gas is used as a reducing agent is a reflection of the trend to clean up steel metallurgy. Rudimentary plasma processes have been in use from the time Siemens invented electric arc furnaces in 1878. The advantages of hooking up intense plasma sources to the metallurgical furnace to exploit the interaction of highly concentrated sources of energy with material is being realised in a new technology called plasma metallurgy [Tsvetkov1995].

This is consistent with the trend of the increasing use of electricity in metallurgy seen in the last few decades with the concomitant improvement in productivity and lesser burden on the environment. Plasma has many unique advantages as a metallurgical tool. High energy density, characteristic of the plasma state due to its high temperatures permits high reaction rates. Energy deposition by the electrons at the anode arc root attachment enhances the efficiency of processes like melting, smelting etc. Both of these properties make compact reactors possible and reduce the capital cost. Plasmas can be manipulated by electromagnetic and gas velocity fields to produce controlled physical configurations and can be used as a medium for in-flight processing free of material boundaries. The power input is independent of the electrical conductivity of the charge in the reactor. Independent control of the feed rate and power allows greater freedom of choice with regards to charge composition, without having to consider the electrical characteristics of the charge. Extremely short time constants of the arc plasma enable fast response in control and protective functions. The reactors are amenable to continuously tapping metal and slag. Using water-cooled tungsten and copper electrodes and eliminating carbon electrodes can minimise product contamination.

The furnace atmosphere can be carefully controlled as it can be almost completely sealed. Plasma furnaces can be operated in oxidising, reducing or inert environments unlike those operated with combustion flames. Reductions of oxides like Chromium, Magnesium, Manganese, Silicon, Titanium, and Aluminium, which are endothermic or require strongly reducing conditions, are appropriate for plasma furnaces. Volatile metals such as Lead, Tin and Zinc can be fumed and recovered by condensation and collection in a bag house. Alloying with Nitrogen in the gas phase is possible without using expensive Nitrogen containing ferroalloys.

The furnace accepts fine materials without going through costly agglomeration route and these can be introduced directly into the hot zone. Typical gas flow rates being low, the feed carryover to the exhaust is also minimised. Rapid reactions, good bath stirring and fluid slags lead to a good metal slag separation. Metallurgical recovery can be improved by the selection of the right slag chemistry, a freedom made possible since the process is independent of the electrical resistance of the slag bath.

Pyrometallurgical Plasma Furnaces

The three fundamental parameters of plasmas that are of particular significance in process metallurgy are temperature, enthalpy and degree of ionisation. Each affects the extent and rate of reaction. The high temperature available in plasmas allows for very rapid rates of reaction. The high enthalpy content as a result of dissociation and ionisation of species is available for endothermic reactions. The presence of molecular, ionised and activated species in a plasma leads to a wide range of additional reaction routes to the desired product. In most cases these routes permit the achievement of reactions not possible in non-activated molecular form and also provide for much faster rate of reaction. All of these factors have the potential to contribute to improved yields and higher rates of reaction in plasma metallurgy.

Based on the three fundamental methods of coupling the energy contained within the plasma to materials, and the nature of the metallurgical charge, three types of pyrometallurgical systems have emerged. These are [Fig.18.1]:

Shaft Furnaces

Where a process gas is heated to very high temperatures normally not attainable by fossil fuels. The high temperature gas then conveys the reaction enthalpy required for the process. Non-transferred torches are used in these applications.

Molten Pool Arc Furnaces

Where the plasma current is transferred to a molten pool of metal and slag. The energy transfer is through the anode attachment zone in the molten surface.

In-flight Plasma Reactors

Where dispersed solids are injected into a plasma jet and the metallurgical processing take place in-flight. This mode of processing is perhaps unique to plasma systems and creates new opportunities in metallurgical processing.

The major impact in commercial applications of plasma systems in process metallurgy has been through the transferred arc furnace route with the main area of application being melting and refining. Multiple plasma torch installations and single graphite electrode installations have both been evolved. There is considerable commercial incentive to develop large capacity plasma torches with extended electrode life to eliminate the costs of graphite electrode wear.

Different types of thermal plasma sources, AC, DC and inductive, have been applied to metallurgical processing. The power of torches range from a few hundred kilowatts to megawatts. A summary of commercialised plasma torches, manufacturers and process capabilities is listed in Table 18.1.

Iron and Steel

Production of iron and steel in their pure or usable alloy form from ores remains the largest component of extractive metallurgy. World crude steel production was 77.8 million tonnes according to August 2003 figures [IISI 2003]. Although iron and steel are perhaps the cheapest metallurgical products, the very large volumes involved mean that even modest savings in production costs have significant impact on the overall economy. Increased cost of energy, regulatory constraints from environmental considerations and the depletion of high grade ores are the drivers for alternative metal extraction technologies. In this scenario, improved energy efficiency and a reduction of electrode consumption can lead to significant improvements in operating cost. The drivers for plasma based metallurgy in Iron and Steel making are the possibility of replacing metallurgical coke with inexpensive coal, exploitation of lower quality Iron ores and the viability of smaller size units. In endothermic chemical reduction of a metal oxide by a reducing gas, reactions will shift in favour of the production of the metal as the temperature is increased. The reaction rates are also influenced by temperature, with a significant increase of the rate constant as the temperature is increased. Greater the endothermic nature of the reaction, the more it will benefit from high temperatures. Pyrometallurgical processes have traditionally depended on fossil fuels as the heat source. These have temperatures limited to in the region of 2000^o C. Temperatures well above this limit can be generated in plasmas thereby opening up areas of process metallurgy not previously accessible to fossil fuel furnace practice.

The two major routes for steel manufacturing are the Blast Furnace Oxygen Converter route and the Direct Reduction process. There are several ways in which plasma technology may be used to enhance the operation of both in addition to providing simpler processes.

Superheating of the hot blast temperature can be achieved by mixing the hot gas plume from a plasma torch with the blast air before injection at the tuyere. Blast air may also be superheated upto 2000^o C and coal injected to generate a reducing hot gas for injection at the tuyere enabling substitution of the metallurgical grade coke by coal injection.

Plasma based process development in blast furnaces operation has been tested upto industrial scale by many European groups; for example, Centre de Recherches Metallurgiques (CRM), SKF Steel Engineering, Soceite du Ferromanganese de Paris (SFPO), etc.

In Direct Reduction of Steel ore (DRI), shaft furnaces are used where the ore contacts the reducing gas in counter current flow in moving or stationary beds. The conversion of the natural gas into hydrogen and carbon monoxide reducing gas is done with catalytic reforming with steam. Thermal plasma can be used to do the conversion directly in the reaction vessel. There are many established DRI processes:

SKF Steel PlasmaRed process is based on the 6 MW magnetised, segmented non-transferred arc generator, which allows long arc columns with high electrical to heat conversion to be created. In this process for direct reduction of Iron ore to sponge Iron, the hot plasma gas and the coal are mixed in the tuyere [Edstrom 1983]. The ore is reduced by carbon monoxide and Hydrogen gas in a continuously operating shaft furnace. The reducing agent can be produced from any carbonaceous fuel-coal, charcoal, peat, heavy fuel oil or natural gas sources.

The process developed by Union Steel Corporation of South Africa (USCO) is based on the reforming of a synthetic gas formed from bituminous coal using three 8 MW Huls arc heaters. The introduction of the plasma energy into a gasification system permits operation independent of oxygen potential and provides efficient energy transfer to the gasifying system. The plant is non-operational since 1987.

Competing with this is the Plasma Smelting-Reduction techniques. Since the Oxygen affinity for Carbon increases with temperature, oxides can be reduced by carbon at high enough temperatures. The plasma assisted processes was originally developed by SKF of Sweden (now ScanArc) using ores and pulverised metal bearing waste in a reducing atmosphere generated by the gasification of fossil fuels in a plasma flame [Herlitz 1984]. The SKF torches are segmented non-transferred devices, which are claimed to have lower erosion, and currents compared to single gap torches [Herlitz 1985]. Plasmasmelt is a two-stage smelting reduction process [Fig.18.2] in which pre-reduction takes place in a fluidised bed and smelting reduction of the pre-reduced material in shaft furnace [Hebbert 1981]. The smelting zone consists of coke column in front of the plasma generators located in the lower part of the coke filled shaft furnace. In this smelting zone, pre-reduced iron ore fines are instantly reduced using coal as the reducing agent. Three plasma torches each with 6 MW capacity are used to produce 35,000 tonnes of metals from 70, 000 tonnes of dust a year [Reid 1984].

Other commercialised processes include Davy McKee Integrated process, ASEA Storakopparberg ELRED Process, Foster Wheeler-Tetronics Expanded Processive Plasma (EPP) Process, University of Minnesota Sustained Shockwave Plasma (SSP) Process and Bethlehem Steel Falling Film Plasma Reactor.

The impact of plasma process in extractive metallurgy has been in their ability to process ores in the fine powder form. Mintek in South Africa have been pioneers in adapting plasma furnace technology for the enrichment of low-grade ores. Recent plasma furnace work at Mintek [MacRae 1985] addresses high intensity smelting, the high temperature reactions at the arc-attachment zone and the application of large-scale plasma systems up to 3.2 MVA capacity.

Ferroalloys

Conventionally ferroalloys are made in submerged arc furnaces which have a fairly high electrical to thermal efficiency i.e. 85-90 per cent and the chemistry of the process is generally self regulating, only limited amounts of high temperature volatile species are lost to the off gases. Submerged arc furnaces have many unattractive features. Their power densities are low, in the range of 0.5 MW/m2. Unreduced iron in the slag (20 per cent by mass in Fe-Mn) results in losses. Low resistance operation gives rise to low power factors. Countries like South Africa and Sweden who have large reserves of ferro alloy reserves ores and abundant resources of carbonaceous reducing agents developed processes based on plasma technology since plasma furnace can be fed with ore fines directly [Jones 1993]. The application of plasma technology to ferro alloys production have evolved through modification or retrofit of an existing furnace with a plasma system as well as through new processes using conventional raw materials or new materials and processes.

The advantages of plasma technology in ferrochrome production are in the use of cheap chromite fines without pre-processing, the use of anthracite or coal as reducing agent and the flexibility in choosing process parameters. Mintek, Middleburg Steel and Alloys and ASEA of Sweden jointly set up a 14 MW DC transferred arc furnace in 1983 to process the chromite fines abundantly available in South Africa. This was upgraded to 40 MW in 1987. The furnace is totally enclosed and the dried chromite fines, mixed with fluxes and coke are fed through the hollow cathode or ports in the furnace roof. The Chromium recovery exceeded 90 per cent, 10-15 per cent more than that possible in submerged arc furnaces [Slatter 1986].

Low, medium and high carbon ferromanganese are important additives in many metallurgical processes. Mintek in collaboration with Voest Alpine have carried out development work on the melting and smelting of ferromanganese alloys in open bath furnaces [Schoukens 1985]. The evaporative loss of manganese was reduced by developing a boot furnace, which was a combination of bath and shaft furnaces [Berger 1987, Muller 1989] built by Voest-Alpine. In the boot furnace the evaporated manganese is condensed in the burden and the thermal loss of hot gases is prevented by using it for pre-heating and partial pre-reduction of the feed material. Ferromanganese fines are used to manufacture ferromanganese-silicon and high carbon ferromanganese in the Freital/Voest-Alpine 10.8 MVA furnace at the Samancore plant in South Africa. The plasma process can also introduce oxygen for decarburisation. The performance of the boot furnace has shown that the plasma process has many advantages over conventional submerged arc process [Glockler 1989]. The primary advantage appears to be the replacement of the two step characteristic of electric submerged arc process with the single step process possible with plasma furnace. These result primarily from the higher power densities of the order of 8GW/m2, which is 3 orders of magnitude larger than that possible with submerged arcs. This effectively leads to unlimited slag superheating enhancing the reaction rats and metal yield.

Davy McKee's Hi-Plas technology is based on the design developed by Gauvin and Kubanek [Gauvin 1984]. A water-cooled sleeve surrounds a substantial part of a 5 MW transferred arc column. Reactants are injected tangentially into the sleeve and are heated by the radiant and convected heat from the arc column. The falling film melts and falls into the molten pool where the reaction is completed.

Smelting and Refining of Steel

The cupola or the vertical shaft furnace has a history of over 200 year of use for melting Iron for foundry casting by the small and medium sized foundries. The conventional technique adopted for making cast Iron in foundries is coke-based cupola where costly metallurgical coke is used. The increasing environmental regulatory pressure and the high cost of air pollution control have forced small foundry operator to shut down. Cupolas can be one of the cheapest and most efficient melting units provided quality inputs, especially high quality coke are used.

Unfortunately, the conventional cupola has many drawbacks. Control of desired metal composition is difficult since the molten metal picks up Carbon and Sulphur. It is not possible to get uniform temperature of the molten metal. Super heating is not possible, thus making effective inoculation difficult. C.I turnings and borings as well as milled steel scrap cannot be charged due to lower melting temperatures in the cupola. Fine scraps such as borings and turnings may be blown out of the cupola if not briquetted, which is an expensive pre-treatment step.

In recent years, many improvements have been made. Combustion efficiency and higher metal temperatures have been obtained by preheating the air blast and by enriching it through the addition of Oxygen. Electric furnaces, usually of the coreless induction type, have tended to replace the low tonnage cupolas. For large tonnage iron melting, cupolas still remain the principal furnaces, even if induction and arc furnaces have replaced many of them, and have to meet to-day's demands of progress in the product and in the process.

The plasma-fired cupola [Fig. 18.3] effectively decouples the melting process from the conditions and materials, which normally affect the chemistry of the product. The first full scale experiments of a plasma fired cupola was made in France by PEUGEOT factory at Sept-Fons, dedicated to manufacture of car engines. The experiments were conducted with a 2.5 MW transportable plasma torch system. The test runs were conducted on a “hot blast” cupola, the blast temperature in the absence of plasma being 400^{o}C. With the torch, the temperature of the blast was increased upto 1000^{o}C. The experiments showed a 30 to 40% increase in production, 30% reduction in effluents volume. After this 3 month experiment, PEUGOT has decided to boost the Sept-Fons cupola with 4 MW torch. This resulted in increase in productivity by 45% and decrease in coke charge.

In 1983, the Electric Power Research Institute (EPRI) in the US brought together Westinghouse and General motors (GM) in a programme to demonstrate a pilot scale plasma fired cupola [EPRI 1986]. General Motors is using a plasma melter to remelt scrap iron at their plant in Defiance, Ohio. The GM melter is 13 feet in diameter. It has a throughput of up to 50 tons per hour. Iron is melted on top of the coke bed at about 1500 C. Water constantly flows down the outside of the cupola to cool the steel shell. Hot blast air is injected into the cupola through the six tuyeres located at the bottom of the melter. A 2 Megawatt Westinghouse plasma torch is mounted onto the end of each tuyere. General Motors is presently using the plasma melter to melt charges consisting of 50%-60 per cent loose cast iron borings.

Tundish is the critical link between the batch steel making and continuous casting. It has significant role in the control of the floatation and assimilation of reaction products in the molten steel into the slag phase, thereby improving the quality of casting. Superheat control of the steel in continuous casting tundish has become necessary to produce high quality steel. Plasma heating of tundishes would be ultimately indispensable for modern continuous casting.

Techniques of tundish heating have been put into operation by a number of steel companies to control the steel temperature in continuos casting tundishes. Controlled uniform temperature throughout the casting cycle gives a more uniform microstructure and reduced inclusions and porosity. Freital in Germany and Voest-Alpine in Austria have developed 15 to 35 ton plasma furnaces for manufacturing high quality steels. Nippon Steel Co. and NKK Co. have used Tetronics plasma torches for tundish heating. Daido Steel in Japan has been operating a Progressive Casting furnace for melting and casting as a competitive process for vacuum arc melting, electroslag refining and electron beam melting [Yasui 1993]. Mannesmann Demag has supplied 2.4 MW AC plasma torch heater to Kobe Steel with a power transfer efficiency of 65 per cent to the melt [Bebber 1989]. Tetronics (UK) and Plasma Energy Corporation supply tundish heating systems.

Application to Specialty Metals

The impact of the plasma technology in the field of smelting, melting and remelting furnaces has been aided by the ability to operate in both inert and reactive environments, thus providing complete control of the atmosphere. Since there are no consumable electrodes, steady state operation for long times is possible. Compact systems that can process materials in a variety of forms at high throughput rates and with relatively high electrical and thermal efficiency are possible.

The high temperature condition prevailing above metal surface during plasma remelting leads to the development of very large temperature gradients ahead of the metal crystallisation front in the ingot. Under these conditions, highly directional growth of grains occurs and factors that cause micro-segregation are suppressed. Ingot metal develops a high degree of chemical homogeneity and structural uniformity. However, micro-segregation can and does occur in ingots, which seem to be related to the defects in the consumable electrode. The process allows remelting with simultaneous de-oxidation of the metal with hydrogen. Since the melting is not done in vacuum there is negligible loss of volatile elements.

Niche applications have been found in the field of scrap melting specially of reactive metals like titanium. A common factor in the production and use of reactive metals, magnetic materials, and certain alloy material, used in aerospace is the high percentage of scrap. Often, no more than 50 per cent of the original material ends up as useful product. Economics dictates the use of the processed scrap. Specialty metals industries have resorted now to the use of plasma melting process to consolidate scrap into remelt electrodes and Plasma hearth refining for the manufacturing of final products in the forms of ingots and rectangular slabs for direct rolling into flat products. Plasma hearth melting technology is readily adaptable for the manufacture of other net shapes such as, hollow ingots and castings.

Titanium based alloys such as Ti-6Al-4V and nickel based superalloys have high strength to weight ratio and are resistant to corrosion and wear at high temperatures. These materials are very reactive and are susceptible to oxidation and contamination under molten conditions. Presence of even small inclusion can act as crack initiation sites. The standard melting route is through vacuum arc or electron beam remelting of sponge or scrap. The purpose of remelting is to float, vaporise of dissolve the low density inclusions, which are oxides and nitrides.

ULVAC in Japan has developed plasma melting systems for Titanium [Bhat 1972]. The use of cold hearth plasma melt refining has been reported by Plasma Energy Corporation (PEC) and Leybold in Ni and Co based superalloys and intermetallic compounds TiAl, Ti3Al and Nb_xAl_y production [Pannen 1989]. The torches are modified PEC designs operated in reverse polarity.

Retech Plasma Systems [Chinnis 1988] have developed cold hearth plasma furnace for the continuous production of Ti ingot from scrap, sponge, turnings etc for subsequent vacuum arc remelting. The feed material is melted in the cold hearth and flows through two refining crucibles before solidification. The Retech systems are in use at Oregon Metallurgical Corporation and Teledyne Allvac [Cowx 1993]

World production of Silicon metal totalled close to a million tonnes in 1999. Brazil, China, Norway and the USA account for 75 per cent of total output. Typically, Silicon is produced in submerged electric arc furnaces through the carbothermic reduction of silicon dioxide [Healy 1970]. The intermediates essential for Silicon extraction are silicon monoxide and silicon carbide. In the arc furnace process, the recovery of Silicon is typically 75-85 per cent of the Silicon in quartz. Dow Corning Corporation, one of the largest consumers of Silicon for the manufacture of silicone products, in collaboration with Voest-Alpine have reported a plasma smelting concept involving the reaction of silicon dioxide and silicon carbide in a shaft furnace [Dosaj 1989]. On plasma heating of an equimolar charge of SiO2 and SiC, silicon is produced along with SiO and CO. The gaseous SiO upon passing through the shaft filled with stoichiometric amounts of Carbon transforms into SiC, which can be fed back into the process. Silicon recovery in excess of 90 per cent was demonstrated in the process.

Ore Enrichment

Titanium metal is a critical component in aerospace applications because of their high strength-to-weight ratios, good toughness, and corrosion resistance. The production of Titanium metal accounts for only 5 per cent of annual Titanium mineral consumption; the rest goes to the Titanium pigment industry. The starting material for pigment production is TiCl4, which is also used for the production of Titanium metal by reducing it with either Sodium in the Hunter process or with Magnesium in the Kroll process.

Rutile, which is about 95 per cent titanium dioxide (TiO_2) can be readily chlorinated. On the other hand, ilmenite ($FeTiO_3$), which contains 50 to 65 per cent TiO_2 can be chlorinated only after benefaction to higher concentration of TiO_2. With the declining reserves of rutile, ilmenite enrichment techniques are increasingly becoming important. Titania slags have high electrical conductivity, which rules out the conventional submerged arc technology for the smelting of ilmenite. The secondary users also impose tight conditions of purity (for example, calcium oxide, 0.2 per cent, magnesium oxide, 1.2 per cent).

Mintek has developed a transferred arc plasma furnace with the molten anode configuration for the smelting of ilmenite [Brent 1987]. Graphite crucible is used to ensure compliance with impurity limits.

Zirconia is produced from the ore zircon (zirconium silicate $ZrSiO_4$). Being chemically inert and refractory, breaking the bond between zirconia and silica requires high temperatures. The decomposition of zircon into zirconia and silica occurs at 1676°C and this occurs below the minimum melting temperature in ZrO_2SiO_2 system. The thermal plasma process developed at a commercial level is known as the Ion Arc process [Thorpe 1971]. A zirconia dissociation reactor is schematically represented in Fig. 18.4. The extended tail flame ensures that the zircon sand was entrained in the arc during its flight from nozzle to the product collector. The residence time of the zircon sand in the hot zone of the plasma arc could be increased by varying the reactor pressure from negative pressure to atmospheric pressure, and finally to positive pressure. So some of the zircon grains might have got dissociated into constituent oxides without going into liquidus temperatures. The quenching of the plasma products within few milliseconds prevents recombination of the dissociation products into zircon. The plasma process, at about 10 kWh/kg of zirconium, offers considerable economic advantages. The process is continuous and most importantly a dense metal and not a sponge is produced which could be continuously cast.

Plasma Cutting of Metal

Plasma arc cutting was invented in 1957 by Robert Gage at Union carbide, by constricting the arc column with a Copper nozzle to produce a narrow arc channel with high speed plasma flow. Present day plasma cutters can tackle a 250 mm plate of stainless steel. Even higher constriction is possible by injecting water radially into the arc. Water produces a steam boundary – Linden Frost Layer - surrounding the hot arc column. These torches are said to have temperatures of the order of 50,000° K, double that of conventional torches.

Air plasma cutting came into industrial applications in the 1960s. Oxygen in the air provided an additional energy source, increasing the cutting speed by 25 per cent over nitrogen plasma cutting. The Tungsten electrodes had to be replaced with Hafnium or Zirconium because of high erosion in the air plasma. Present day air plasma cutters operate with Nitrogen plasma and an outer air layer.

Very recently technology has been made available for combined plasma and water cutting for developing high quality cut surface in stainless steels. Also plasma cutting improvements in achievement of higher production outputs in continuous casting operations of both thick section and thin section slabs of alloy steels have been realised. Nevertheless, improvements in cutting efficiency and higher degree of automation in the plasma cutting systems are constantly being sought. A recent development is the use of microwave plasma sources modified for cutting applications. The cutting quality is claimed to be comparable to what is achieved in laser cutting, with much lower cost. Very few suppliers of plasma equipment worldwide seem to be putting the required efforts to further improve the performance of plasma systems.

Microplasma welding systems have been developed for fusion welding of extremely thin bellows and closed sealing of packages in the production of electronic parts. Microplasma torch systems are also used for the encapsulation of pacemakers and other biomedical devices. Because of their compact size microplasma systems have found special applications in the construction of structures in space and for joining wires and thin tubular components.

Applications to Engineering Ceramics

Ceramics date back to the beginning of human civilisation. Synthetic ceramics encompass all metal oxides and carbides up to number 14 in the periodic table. Engineering ceramics attain the hardness rating of 1,200-1,900 Vickers scale, or 7.5-8 on Mohs scale.

High technology ceramics are new types of materials that surpass earlier ceramics in strength, hardness, lightweight, or improved heat resistance. For example, ceramic powders can now be made from particles of absolutely uniform size. When sintered, these powders produce ceramics that are far less vulnerable to fracture or thermal shock than ordinary ceramics. Added to a matrix of metal or ceramic, thin ceramic fibres increase the tensile strength of the material. New super-hard ceramics make excellent cutting tools and bearings.

Thermal plasmas are characterised by their high enthalpy and quenching rates. The high temperature available in the thermal plasma can vaporise any material and enhance reaction kinetics by several orders of magnitude. The rapid quenching of the particles can be used for generation of fine powders. This technique has been exploited in the synthesis of ceramic powders namely aluminium nitride, silicon carbide, titanium carbide, aluminium oxide etc. The purity of the final product is least influenced by the plasma source compared to any other competitive techniques. It also eliminates many intermediates steps which are used in the conventional techniques thus generates less waste.

The production and processing of fine particles (nanometer to 100 micrometer) represents one of the important areas in plasma processing. These particles have an important resource for today's technology, in powder metallurgy, which has grown to be a powerful manufacturing tool. Today, fine powders are used for making structural components frequently as a higher quality and less expensive product than components made by earlier technologies. A typical example is the sintering of ceramic materials into structural components for advanced heat engines. For ceramics, sintering is the only method for product manipulation, for by sintering one can bypass the melting process entirely. Such materials usually sinter at 70-90 per cent of the melting temperature.

The process used for generating particles determines the degree of sinterability of the powder, because the process determines the particle shape and size distribution. Thermal plasmas can produce very small and pure powders aiding towards the goal of pressure less sintering. Unfortunately such small particles tend to contaminate easily - some materials form an oxide coating a few monolayers thick. Fine Aluminium powder for example oxidises easily when exposed to atmosphere air and drastically alters electrical and thermal properties.

Thermal plasmas offer distinct advantage of providing essentially one step process avoiding the multitude of steps required for producing particles with conventional methods. Fine powders are usually high price items manufactured from low cost materials. Chemical and physical properties are distinctly changed and improved compared to bulk materials.

In the past few years, materials scientists have shown that materials composed of nanometer-size grains or crystallites often have materials properties distinctly different, and often much more useful, than more coarse grained material of the same composition. Thus, for example, such "nanostructured" ceramics are tougher and less brittle than coarser grained equivalents and some show plastic flow or elastic properties at elevated temperatures. Nanostructured metals are significantly harder than coarser grained metals, and nanostructured materials are often more active catalytically than their conventional equivalents. Synthesis in high-temperature thermal plasma meets many of the requirements for the production of advanced materials, including nanostructured materials, and increasing R&D effort is being devoted to exploring its applications in the materials processing industry. Scientists at the University of Idaho have, over the last 7 years, developed novel thermal plasma processing technology, which promises to be widely applicable to the production of nanostructured and other advanced materials [Taylor 1994].

Plasma processing has inherent advantages in the production of advanced materials. Reaction temperatures much higher than can be achieved using fossil fuels can be attained. These high temperatures dissociate any compounds fed into the plasma, and vaporise virtually all elements, so that all reactions take place in the gas phase. The high temperatures, and the presence of chemically reactive species formed in the plasma, may accelerate chemical reactions by several orders of magnitude. Residence time in the high-temperature zone is short and controllable. The ability to quench rapidly from very high temperatures produces very small spherical particles, typically a few tens of nanometers to a few hundred nanometers in diameter. By suitable choice of feed gases, reactions can take place in an inert atmosphere, or a suitable oxidising, reducing or other reactive environment. Starting materials can be fed to the plasma reactors in either gaseous or powdered form. Generally, reactants can be chosen to avoid the production of corrosive or toxic by-products, e.g., metals can be fed as oxides rather than chlorides.

Silicon carbide (SiC) was formed by reacting silica (SiO_2) with methane (CH_4). Spherical particles 200-300 nm in diameter of highly pure SiC were produced. Boron carbide, B_4C, was similarly formed by reacting boric oxide, B_2O_3, with methane. Titanium carbide (TiC) was formed from titanium dioxide (TiO_2) and methane in the form of 200-400 nm diameter spherical particles. Titanium carbide was also formed directly from ilmenite ($FeTiO_3$, a common Ti-containing mineral and methane, without any preliminary purification or refining of the mineral ore. The Fe-containing compounds were removed from the reaction product by acid leaching. Roughly spherical submicron particles resulted. This process may be a very economical method for the preparation of TiC, although the material will contain some contaminants from impurities in the ilmenite.

Other materials processed by the plasma route include Zirconium carbide (ZiC) formed from zircon sand ($ZrSiO_4$), Titanium diboride (TiB_2) by reaction of TiO_2, B_2O_3, and methane, Zirconium diboride (ZiB_2) by the reaction of ZrO_2, B_2O_3 and methane, Silicon nitride (Si_3N_4) from SiO_2 and ammonia etc.

Spheroidization and Densification

Spheroidization is a process of converting irregular ceramic or metal powders into spherical shape. Spherical particles flow more smoothly compared to irregular particles and hence such powders find applications in plasma spray coating systems, and where the powders are used as a medium to mix pigments and chemical slurries. High temperature plasma flows can be used for in-flight melting and spheroidization. Other features imparted during the spheroidization process are densification, porosity reduction and surface finish.

Spheroidization of irregular alumina particles using high enthalpy in-flight thermal plasma reactor has been done using the in-flight reactor described for Zirconium dissociation process. The electric arc was struck between the vertical cathode and the anode carbon rods radially disposed in a horizontal plane at an angle of 120. The feed arrangement is housed at the top of the reactor and conveys alumina particles (125 size) into the cathode-anode gap of the plasma torch. The torch was connected to a 50 kW power supply. One of the main advantages of plasma in-flight reactor is that the plasma tail flame extends for about 3 feet. When the material in the powder form was fed through a feeder arrangement around the nozzle, the powder enters the core of the flame and travels inside the flame for sufficient length of time. A carrier gas is used to inject the particles into the core of the plasma, which is normally difficult due to the high viscosity of the plasma. The velocity of the feed is adjusted so that the freefalling particles have enough residence time to be completely melted. Once the molten particles exit the plasma region, they immediately condense and form spherical droplets. A photograph of the spheroidized alumina particles is given in Fig. 18.5. The treated powder was collected at the bottom of the reactor.

The spheroidization process can be integrated with purification of the powder of selective impurities, which have a low vaporization temperature compared to the bulk material. Tekna plasma systems [Tekna], a commercial supplier of plasma densification systems using induction plasma torches up to 100 kW capacity claim purification by a factor of 100.

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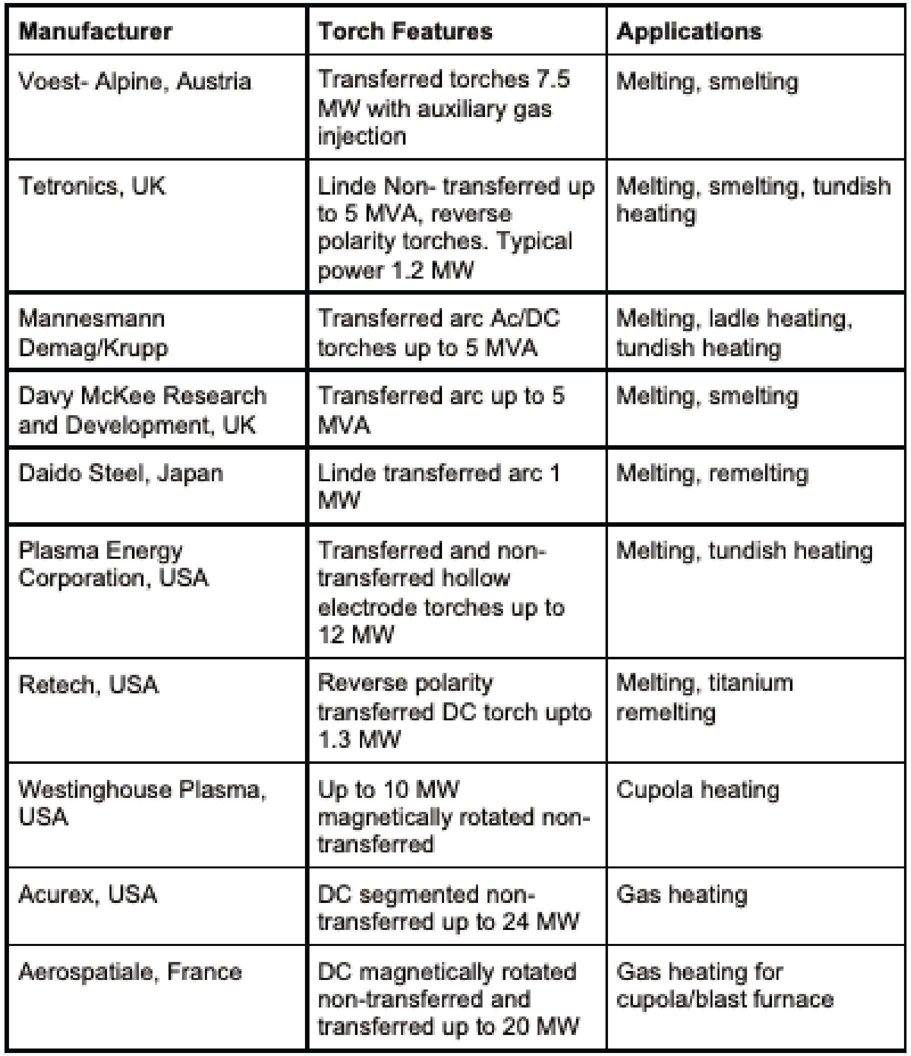
Table 18.1: Plasma Torches for Metallurgical Applications



Manufacturer	**Torch Features**	**Applications**
Voest- Alpine, Austria	Transferred torches 7.5 MW with auxiliary gas injection	Melting, smelting
Tetronics, UK	Linde Non- transferred up to 5 MVA, reverse polarity torches. Typical power 1.2 MW	Melting, smelting, tundish heating
Mannesmann Demag/Krupp	Transferred arc Ac/DC torches up to 5 MVA	Melting, ladle heating, tundish heating
Davy McKee Research and Development, UK	Transferred arc up to 5 MVA	Melting, smelting
Daido Steel, Japan	Linde transferred arc 1 MW	Melting, remelting
Plasma Energy Corporation, USA	Transferred and non-transferred hollow electrode torches up to 12 MW	Melting, tundish heating
Retech, USA	Reverse polarity transferred DC torch upto 1.3 MW	Melting, titanium remelting
Westinghouse Plasma, USA	Up to 10 MW magnetically rotated non-transferred	Cupola heating
Acurex, USA	DC segmented non-transferred up to 24 MW	Gas heating
Aerospatiale, France	DC magnetically rotated non-transferred and transferred up to 20 MW	Gas heating for cupola/blast furnace

Table 18.2: Cost comparison between plasma and induction heating in cupola

		Conventional		Plasma	
Item		Qty	Cost*	Qty	Cost
Pig iron	@8,000/ton	500 kg	4,000.00	200 kg	1,600.00
C.I scrap	@6,600/ton	300 kg	2,000.00		
C.I borings	@5,000/ton			600 kg	3,000.00
Foundry returns	@ 6,000/ton	200 kg	1,200.00	200 kg	1,200.00
Indian coke	@4,000/ton	160 kg	640.00	25 kg	100.00
Chinese coke	@6,000/kg**	100 kg	600.00		
Other materials			50.00		50.00
Power		3 units	15.00	200 units	1,000.00
Total			8,490.00		6,950.00

- *In Indian Rupee (1 $ = Re 45)
- ** 12% ash content

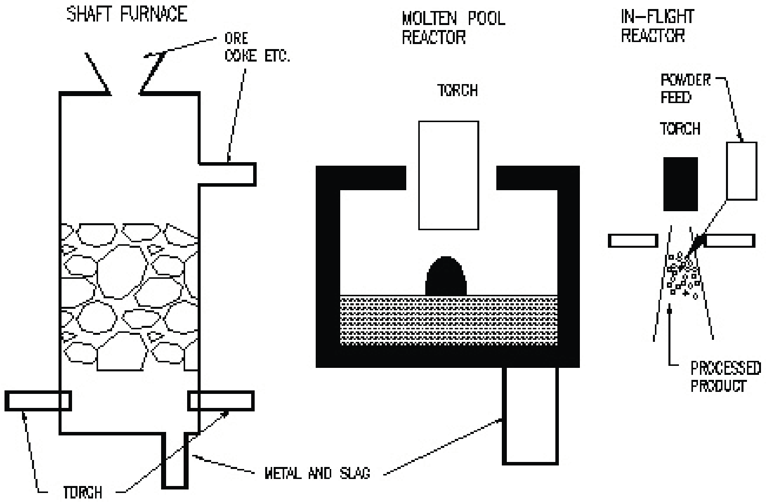


Fig. 18.1. Three fundamental pyrometallurgical configurations

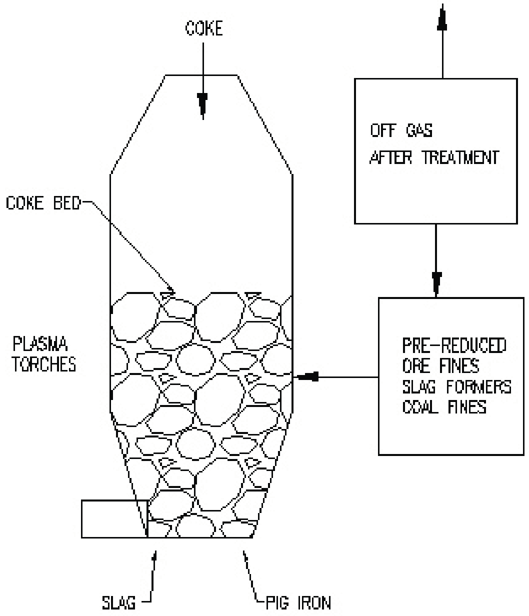


Fig. 18.2. Schematic diagram of the plasmasmelt process

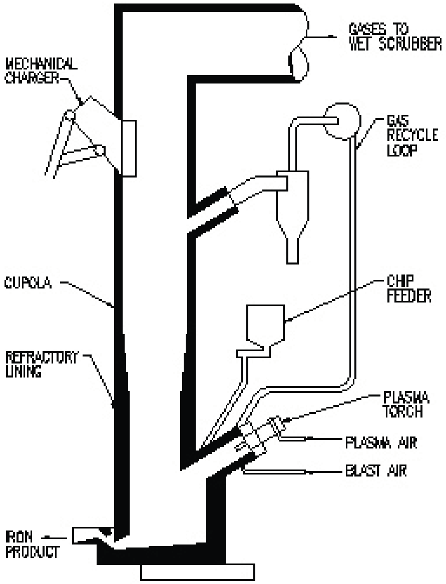


Fig. 18.3. Schematic diagram of the plasma fired cupola

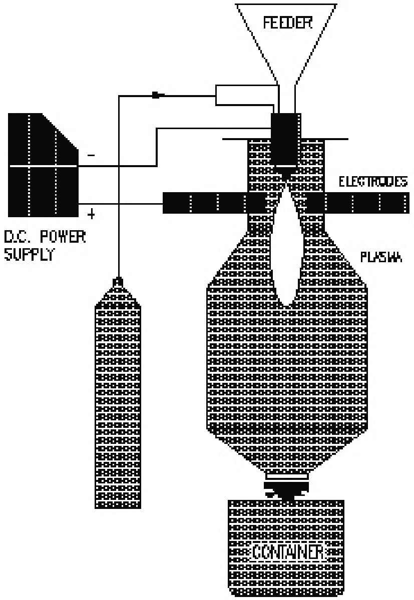


Fig. 18.4. In-flight reactor for zirconia dissociation

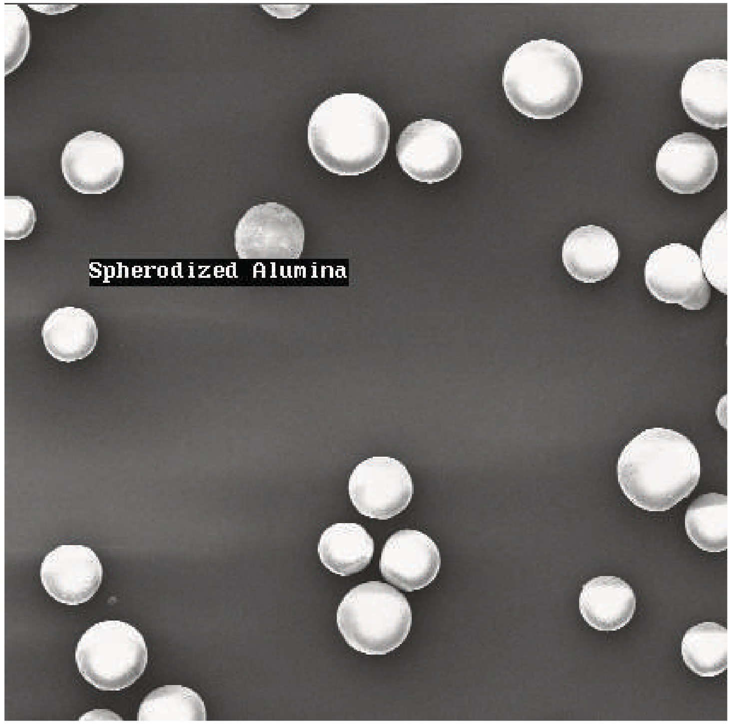


Fig. 18.5. Photograph of alumina particles spheroidised in an in-flight plasma reactor

19. Wealth from Waste

Plasma Assisted Recycling Processes

Modern concepts in industrial ecology and sustainable manufacturing promote recycling of industrial waste to recover value. Thermal and non-equilibrium plasmas are acquiring an important role as an enabler of this process. This chapter discusses some specific applications where energy and material are recovered from waste using plasma-based processes.

Industrial Ecology

Historically the relationship between champions of economic development and protagonists of environmental protection has been antagonistic. Traditionally governments have relied largely on regulatory measures to keep industry in check and to meet laid-down standards of environmental protection. Where regulation is not implemented, public and judicial activism has been exploited to resolve the conflict. The “Green Movement” has also become synonymous with a deep distrust of modern technology.

New concepts of industrial ecology and sustainable development promote recycling and the use of waste from one industry as the raw material of another are needed to resolve this conflict. Industrial ecology [Ausubel] imitates nature in minimising harmful waste and in maximizing the economical use of waste and also of products at the ends of their lives as inputs to other processes and industries [Fig. 19.1]. The tools of industrial ecology are zero emission, materials substitution, dematerialization, decarbonisation etc.

An interesting example of this approach is the seaside Danish industrial town of Kalundborg. A complex industrial symbiosis has developed over the past 30 years as firms sought to make economical usage of the by-products, partly to minimise the cost of complying with ever-stricter environmental regulations [Grann 1997]. The waste steam from the Asnaes power station is supplied to nearby industries and homes. Gyproc uses calcium sulphate, industrial gypsum, a by-product of the sulphur-dioxide scrubber. The fly ash and clinker from the power station is used in building roads and producing cement. The Statoil refinery supplies ethane and methane to Gyproc for burning its gypsum board ovens. The flare gas is supplied to Asnaes, which reduces its coal consumption. Waste sulphur from the Statoil plant is pumped to Kemira to make sulphuric acid. Statoil sends the hot wastewater to Asnaes for use in industrial cleaning. Novo Nordisk, a pharmaceutical manufacturer supplies its nutrient rich sludge to nearby farms. All this has happened with the industries themselves working out the mutual dependence scheme without regulatory or external intervention. The interaction is schematically shown in Fig. 19.2.

In 1994, the United Nations University proposed the concept of Zero Emission as an ideal in which the human race places zero stress on the environment by minimising resource consumption and maximising recycling of waste [UNU]. The Zero Emissions Research Initiative seeks to improve the profitability of manufacturing while reducing its environmental impact by finding interdependence between consumers and industries. Waste created in one sector is recycled into resources that benefit another sector forming multi-industry clusters of factories. The resulting interrelationships generate business opportunities geared to Zero Emission objectives. This is in contrast to the conventional "end-of-pipe" approach, where consumers and industries generate waste, which is sent outside for processing. ZERI is an international effort to bring together industry, policymakers and researchers to foster the necessary technological breakthroughs needed to achieve waste-free manufacturing, i.e. no waste output into the air, water or in solid form.

ZERI represents a conceptual shift from traditional models in which industrial wastes are considered a necessary evil, to integrated systems in which everything is valorised. It heralds the start of the next industrial revolution in which industry mimics nature's sustainable cycles and minimalism, learning to do more with what the Earth produces. Zero Emissions envisages all industrial inputs being used in the final products or converted into value-added inputs for other industries or processes. In this way, industries will reorganise into "clusters" such that each industry's wastes / by-products are fully matched with others' input requirements, and the integrated whole produces no waste of any kind.

From an environmental perspective, the elimination of waste represents the ultimate solution to pollution problems that threaten ecosystems at both local and global levels. In addition, full use of raw materials; accompanied by a shift towards renewable sources, means that the utilisation of the earth's resources can be brought back to sustainable levels. For industry, Zero Emissions means greater competitiveness and efficiency. Zero Emissions can therefore be viewed as a new standard of efficiency, much like Total Quality Management (zero defects) and Just-In-Time (zero inventory). The full use of raw materials creates new industries and generates jobs even as it raises productivity. It provides the means to feed, clothe and house large populations without destroying the ability of future generations to do the same.

From all these considerations, there emerges the concept of 'clean technology'. A clean technology is one where source reduction or recycling methods applied to eliminate or significantly reduce the amount of any hazardous substance, pollutant, or contaminant released to the environment. Source reduction aims at reductions in the volume of wastes generated, and source control (input material changes, technology changes, or improved operating practices). So-called "by-product management" is closing the loop of materials use and reuse and is challenging the very definition of "waste" itself. Clean technologies include process changes that reduce the toxicity or environmental impact of wastes or emissions as well as recycling methods. Plasma based processes have already demonstrated their potential as clean technology in the context of surface engineering and in controlling air pollution from power stations and mobile sources.

Energy Recovery from Organic Waste

It is estimated that India produces 36.5 million tonnes of municipal waste every year [India Country Report]. About 70% of this is biodegradable or organic waste like food waste, plastics, textiles etc. The energy content can be assumed to be of the order of 3000 kilojoule per kilogram, [Bhoyar 1996]. The rule of thumb is that 100 tonnes of msw can generate 1-1.5 MW of electricity.

The traditional method of MSW treatment has been landfills where a combination of aerobic and anaerobic composting decomposes the material and releases gases such as methane, which are recoverable. The capacities per plant are typically 10 TPA. The footprint size and the noxious smells associated with gas emissions confine these processes to non-urban areas.

Gasification and pyrolysis are thermochemical processes taking place at temperatures above 400°C, which decomposes carbonaceous material. In the absence of Oxygen the process is called pyrolysis. With partial oxidation sufficient to sustain heat while restricting the oxygen supply so much that flame-combustion is inhibited, the process is called gasification. In this manner solid material is split into substances that can be used as fuels. Gasification aims at a partial break-down of the organic molecules leaving a gaseous product usually referred to as synthesis gas or syngas.

Pyrolysis at low temperature is known as 'slow pyrolysis' and converts Carbon to charcoal. As process temperature increases 'fast pyrolysis' takes place and the product can become liquid or gas. Carbonaceous waste, such as MSW, produces a fuel gas with a heating value one-quarter to one-third of natural gas. The gaseous products formed during the conventional pyrolysis of organic waste are Hydrogen, carbon monoxide, carbon dioxide, methane, C_2 hydrocarbons such as ethane, acetylene and ethylene, C_3: propane and propylene, C_4: iso-butane, n-butane, Butylene, Butadiene, C_5, C_6: hexane, aromatic hydrocarbons like benzene, soot and some oily products.

$$C_6H_{10}O_5 + \text{Heat} \quad CH_4 + 2CO + [3H_2O \quad + 3C] \quad CH_4 + 2CO + H_2O \qquad \ldots \text{(i)}$$

$$\text{-}CH_2\text{-}CH_2\text{-} + H_2O/O_2 + \text{Heat} \quad 2H_2 + 2CO \qquad \ldots \text{(ii)}$$

$$CH_4 + H_2O \quad CO + 3H_2 \qquad \ldots\text{(iii)}$$

$$C + H_2O \quad CO + H_2 \qquad \ldots\text{(iv)}$$

The compositions of the gaseous mixture obtained under slow and fast pyrolysis, measured with gas chromatography instrument are shown in Fig. 19.3.

Commercial systems use both pyrolysis and gasification methods of waste regeneration. The latter is a two step process where in the first stage, typically in the 400-800°C range, the decomposition is into heavy hydrocarbons and tar forming components such as naphthenes [Hetland 2001]. In the second, high temperature stage at typically 3000-5000 °C, the gas decomposes entirely into CO and H_2. Each reactor consists of a feeder, a reactor vessel, one or more plasma torches with their associated power supplies and controls, pollution abatement and monitoring hardware plus assorted slag and gas handling facilities. Large facilities use typically 700 kW to process a tonne of MSW.

The produced fuel gas is a low calorific value gas (LCV) with a heat value of about 4 MJ/m^3. The content of carbon monoxide plus Hydrogen amounts to 35-40 per cent. This gas can be used for:

1. Combustion in a boiler for the production of steam for internal processing and/or other external purposes, or for generation of electricity through a steam turbine;
2. Combustion directly in a gas turbine or a gas engine for the production of electricity;
3. Production of methanol;
4. Extraction of both hydrogen and carbon monoxide as discrete

industrial fuel gases.

A typical co-generation system is based on a steam turbine, driven by a dual-fuel (product gas plus LNG or diesel) boiler. The syngas has to be processed to remove Chlorine, Sulphur, Mercury and other elements, which are potentially harmful to the turbine. This technology is already in place in coal gasification plants and petrochemical industry. The problem is that the heterogeneity of MSW, both in moisture content and composition with variable calorific value makes it imperative that the use of syngas in turbine has to be supplemented with natural gas to generate a reasonably steady energy output. The overall efficiency of the system may be improved if energy is also recovered from the heat in the product gas, the torch cooling water and the scrubber water. This involves adding one or more heat recovery steam generators into the system. Alternative designs (gas-fired reciprocating engine, gas turbine, etc) are also feasible. The selection of a specific design can be influenced by factors such as projected capital cost, projected maintenance cost, available maintenance infrastructure, and projected energy conversion efficiency.

The production of electricity from the product gas is gaining substantial favour. The energy in the product gas coupled with substantial amounts of recoverable sensible heat from the process can generally produce sufficient electricity to drive the process. This configuration also incorporates the recovery of sensible heat from three sources: the product gas, the closed loop water systems for pollution abatement and torch cooling. The provision of dual fuel into the boiler provides versatility for increased amounts of power generation as required.

The primary solid residue in MSW disposal is a glassy slag resulting from the melting of the inorganic component of the waste. The slag effectively traps toxic residues like Cadmium, Lead, Chlorine etc. permanently from leaching out. The emissions relevant to environmental regulations are sulphur dioxide, hydrogen chloride, carbon monoxide and volatile organic compounds, which have to be under prescribed limits.

Hitachi Metals Ltd have set up one of the largest gasifier systems for 24 TPD MSW using 600 kW Westinghouse torches at Yoshi in Japan. Another large plant to treat 336 TPD is under construction in Rome. However, small-scale plants are also becoming viable. In the county of Melhus 20 km south of the city of Trondheim, Norway, a small-scale cogeneration plant is being planned together with a local district-heating network [Bakken 2001]. The plant is fuelled by 5000 tonnes per year municipal solid waste (MSW) and will supply 17 GWh/year heat to the district heating system and 6 GWh/year electricity to the local grid.

Metal Recovery from Steel Plant Dust

In the production of Carbon and stainless steel, the amount of dust generated is typically 15 to 20 kilogram per ton of the production. The metal content is in the form of oxides and the dust itself may be considered as a complex ore. Approximately 1 million tonnes of steel dust is reported to be produced in the US in 1995.

In many countries the EAF dust is now considered environmentally hazardous. In the US the Environmental Protection Agency (EPA) set of 8-8-88 as the date beyond which these dusts could no longer be dumped as landfill. Similar restrictions have also appeared in Europe and Japan. The metal components cannot be separated by physical means and the chemical leaching is only partially successful. A pyrometallurgical smelting process is now considered the most effective process for metal recovery and in the treatment, it produces a stable non-toxic slag.

EAF dust from stainless steel manufacturing has low Zinc (less than 15 per cent ZnO) while dust from Carbon steel making contains higher fraction (greater than 15 per cent ZnO). The dust may also be categorised according to their content of alloying elements like Ni, Cr, Mo and Mn. Alloy steel dusts have to be processed to reduce chromium in the slag for further disposal. The composition EAF steel fume is given in table 19.1.

The Zinc and Lead content in the dust is generated from galvanised scrap used in the furnace. Secondary treatment of dust to recover the contained Zinc was rarely considered a viable option by conventional technologies because the material is generally low grade and contaminated species such as halides; alkali oxides and Iron make recovery of Zinc technically difficult [Herlitz 1986]. The dusts are present in a very fine particulate state, which also make them difficult to handle.

Plasma furnaces are capable of handling a wide range of dusts of varying particle size and chemical composition directly without the aid of expensive agglomeration. The power input to the furnace is controllable and is independent of furnace atmosphere and slag chemistry. The potential to condense valuable metals directly from the offgas is the other advantages of the plasma process.

Shaft furnaces are generally used for Zinc recovery. The flow chart of a typical plasma dust treatment plant is given in Fig. 19.4. In operation, the dust is pre-treated to remove halogens and other undesirable components. The product is then mixed with carbonaceous material such as coal or charcoal and flux and introduced into the furnace from the top. This material is heated as it descends through the furnace atmosphere before rapid dissolution in the melt. The reactions within the plasma furnace at the slag/gas phase, which lead to zinc extraction, are [Dal 1993]:

(1) $ZnO + CO = Zn(g) + CO_2$

(2) $2FeO + ZnO = Zn\ (g) + Fe_2O_3$

Within the melt the following reactions take place:

(3) $Fe_2O_3 + CO = 2FeO + CO_2$

(4) $CO_2 + C = 2CO$

Reaction 3 ensures that ferrous Iron is produced sufficiently so that reaction 2 can proceed to the right. Reaction 4 ensures that the partial pressure of CO is maintained high for reaction 1 to proceed. The metal oxides are selectively reduced carbothermically, to volatilise the Zinc, Lead and Cadmium present in the dust.

The Carbon balance is controlled to produce a non-toxic discharge slag. The amount of coke is determined by the requirement that the CO/CO_2 partial pressure ratio is high enough to ensure that vapour phase Zinc is not oxidised before reaching the condenser [Rankin 1990]. The furnace is operated at a temperature of around 1500° C. High temperatures ensure that the reacting species (Zn, Fe) diffuse fast and the slag is well mixed and fluid. At higher temperatures Zinc oxide reduction becomes favourable compared to Iron reduction. At temperatures below 1000° C, Zinc oxidation by CO_2 becomes excessive.

The metal vapours are condensed in a splash condenser. The gases from the condenser are burned in a combustion chamber and cooled with excess air prior to cleaning in a bag house. The Zinc rich baghouse fume may be recycled to the furnace. The cleaned exhaust gases are vented to the atmosphere.

A number of manufacturers have developed plasma-assisted technology for the treatment of the dust. Tetronics Research and Development Co. Ltd., U.K. has developed its Extended Processing Plasma concept for EAF dust treatment. The resultant ferroalloy having average composition Cr (20.5), Ni (5.8), Mn (3.6), Mo (2.3) and Fe (60.1) per cent was smelted and the residual baghouse dust was sufficiently ZnO-rich (38.8 per cent) for sale to Zn producers or can be treated on the site to recover Zinc. A significant advance was made when the Center for Metal Production, on behalf of a group of 22 US companies chose the Tetronics process for a series of five trials, incorporating both the metal quality and environmental legislation requirements. The Tetronics system has also been modified to use graphite cathodes because of their inherent capacity for higher power operation and the improved reliability because of the lack of necessity for water-cooling.

SKF's Plasmadust process was developed in the 80's. The Zinc recovered is usually of prime western grade with a Zn content of 98 per cent. The plant at Landskrona, Sweden was built for Scandust AB uses coke-filled shaft furnace as the reactor, housing three 6-MW plasma generators. It is operated for the processing of dust from a nearby steel plant with a capacity of 40,000 tonnes per year. The Zinc recovery operation was suspended in 1987 because of economics, but the Scandust experts now claim that it would be economical at present.

Council for Mineral Technology (Mintek), South Africa has developed the process called `Enviroplas process' [Schoukens 1993], based on the reduction of selected metal oxides using a carbonaceous reducing agent, which can treat EAF dust, alloy steel dust or a mixture of both. When dust from a stainless-steel operation is smelted, another objective is to recover Chromium and Nickel into a crude ferroalloy. A 3 MW demonstration plant, including a plasma-arc furnace and an ISP (Imperial Smelting Processes Ltd, UK) Lead-splash condenser was successfully commissioned during 1994/95 using about 1000 tonne of Lead blast-furnace slag [Schoukens 1995]. Mintek has also extended this process for the recovery of Cobalt, Nickel, and Platinum group metals from copper or Nickel smelters [Jones 1993].

Westinghouse Corporation in collaboration with Philip Environmental Inc. has developed the Zinc Iron Plasma Process (ZIPP) to maximise the recycling of EAF dust into commodity raw materials for industrial markets. Through the application of Westinghouse plasma torch technology and a vertical shaft furnace, briquetted EAF dust is combined with coke, flux, and scrap steel to provide pig iron, zinc oxide, small amounts of lead oxide and silicate slag. The zinc oxide is converted to Zinc powder and introduced into an electric melter to produce high-grade Zinc ingots. The design of the recovery facility is for 24,000 tons per year of high purity Zinc. The ZIPP process is a source of pig Iron, and with scrap Iron supply becoming tighter over the next five years, this new source will be greatly needed.

Aluminium Dross

Dross is a waste bye-product formed whenever hot metal is exposed to air and consists of oxides and nitrides mixed with metal. A typical example is the dross formed from the Aluminium metal production process. When molten Aluminium is exposed to ambient air, part of the metallic Aluminium is oxidised. The oxides that are formed freeze at high temperature than the freezing temperature of molten Aluminium. The metallic Aluminium and other metal impurities freeze on the oxides, generating Aluminium dross. The dross may contain as much as 50 per cent Aluminium metal.

The separation of the Aluminium metal from the dross, traditionally done in a rotary salt furnace is a complex process. It was necessary to add various salts to lower the temperature at which the aluminum metal separates from the oxides and to prevent Aluminium from oxidizing. The salt addition formed salt contaminated wastes, called salt cake, which complicates the disposal process. The Alcan plasma process [Lavoie 1995], developed by Alcan International Ltd., Canada uses Westinghouse 1.5 MW plasma torches to heat the dross to recover Aluminium metal from the dross. The process is very simple and no salt or other additive is required to isolate the metal from the dross. The furnace is rotated to tumble and expose the dross to the plasma flame. Air is used as the plasma gas. The product gas from the furnace is exhausted to the open air via a particulate filter. The unique ability of the plasma torch to heat materials to very high temperature is utilised in the process. Nearly 100 per cent of the metallic Aluminium is recovered. One plant is at Alcan [Lavoie 1990] in Canada and another plant is at the Plasma Processing Corporation in West Virginia. The PPC plant processes approximately 100 million pounds of dross per year, recovering about 50 million pounds of Aluminium per year. The by-product of the Alcan dross treatment process is Noval, containing alumina, aluminium nitride, magnesium spinel etc. many by-products such as sodium aluminate, brown fused alumina etc also have commercial value.

Ferrochrome from Tannery Waste

Chromium is an essential element in the leather industry, used to stabilise protein collagens in animal hides and skin. Although hexavalent Chromium is an environmentally hazardous material, in the absence of an alternative process, tannery industry will continue to depend on Chromium and produce Chromium-laden waste.

PyroArc developed a process based on plasma pyrolysis in a shaft furnace treating tannery waste by adding iron to favour the formation of ferrochrome and has supplied the reactor to Borge Garveri AS in Norway in 2001. The Chromium content is recovered as molten ferrochrome with no hexavalent Chromium left as residue.

Glass Ceramics from Fly Ash

In the developed world, a large and increasing proportion of combustible solid waste is incinerated in order to reduce their mass and volume to lower landfill costs and also generate electrical power to offset treatment costs. Over 100 million tonnes of municipal solid waste (MSW) and 4 million tonnes of sewage sludge waste (SSW) are burned annually worldwide. The residue from incineration consists of a bottom slag and fly ash. The ashes produced from incineration (around 15-20 per cent by mass of the feed material), are of low bulk density and contain leachable toxic heavy metal species and persistent organics. At present, the majority of incinerator ashes are landfilled. However, in many countries, this situation is liable to change, as suitable landfill sites become increasingly scarce and the laws regulating waste dumping become more stringent.

Fly ash must be decontaminated and detoxified because it contains significant concentrations of heavy metals such as Lead, Chromium, Copper and Zinc [Kirby 1993]. If fly ash is melted at temperatures above 1300^{o}C with proper amount of glass forming additives, inert glass can be produced and organic compounds can be destroyed [Romero 1999]. Fig.19.5 shows the ternary diagram, which shows glass-forming regions in the presence of SiO_2 and MgO. Most fly ashes contain elements like silica and aluminium in amounts favourable to vitrification. Alumina improves the stability of the glassy slag and improves resistance to chemical agents. Oxides like Na_2O, K_2O, CaO and MgO act as modifiers and lower the vitrification temperature. At low temperatures, heavy metals can be stabilized by incorporation into the glass matrix [Park 2002]. As the temperature is raised, they can be volatilized for collection.

Tetronics has developed a commercial scale twin DC plasma arc heating system for the vitrification of waste ashes generated in the incineration of MSW and SSW capable of treating 30 Tonnes per day. Both hollow graphite electrodes or water cooled plasma torches can be used. The product can be utilized in a number of building and other material applications thereby further enhancing the process economics.

For the MSW and SSW grate ashes, around 92-95-wt per cent of the ash feed is converted to slag. In the case of MSW fly ash, slag yields in the region of 80 wt per cent were achieved. This lower recovery rate is largely due to the high content of chloride, sulphate and other volatiles present in the feed. All leachates from the slags fell below concentrations permitted by legislation. The toxic equivalent (TE) concentration of dioxins and furans in the initial MSW fly ash was 5-10 ng/g, which was reduced to 0.002 ng/ g in the secondary fume from the plasma reactor.

The VitroArc process developed by ScanArc Plasma Technologies converts fly ash into a vitrified black, glassy slag that is stable and non-leachable. Heavy metals are recovered in the process. They have built a vitrification facility in Sweden capable of treating one ton fly ash per day. The slag contains about 14 per cent ferrous metals and one percent non-ferrous, such as Copper, Aluminum, and Lead. These metals are worth recovering because they have a market value and, after they are extracted, the clinker can be used as a construction aggregate.

Depolymerisation of Waste Polypropylene

The municipal waste contains on the average 10 per cent plastics. In 1999, the United States generated close to 10 million tonnes of plastics in the municipal solid waste stream [EPA website]. Plastics are polymers are made from monomers derived from petroleum. Conventional chemical treatments cannot recover the monomers because of their chemical complexity.

Monomers can be recovered by thermal decomposition in thermal plasma followed by rapid quenching. Depolymerisation is one of pyrolytic reactions [Albright 1983] initiated by abstracting a Hydrogen atom or by homolytic cleavage of a Carbon-Carbon bond. Formation of Carbon soot and Hydrogen must be quenched to favour depolymerisation. A current limitation of this process is the lack of understanding of reactions occurring in the plasma. Treatment of mixed polymers typical of the actual MSW stream composition would involve a large number of simultaneous decomposition and rearrangement reactions, which makes the process very complex.

Recent work at Drexel University [Guddeti 2000] using an inductive plasma torch show that high average temperature of particles would form greater number of primary radicals and the β scission of these radicals would yield to greater propylene concentration. Mass balance runs show that greater than 78 per cent conversion of PP into gaseous products was achieved with the products predominantly propylene (97 per cent) and the balance methane, ethylene, acetylene and butane. The monomer products can be recovered or directly used for creating plasma polymerisation coatings.

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Table 19.1: Chemical composition of EAF dust

Metal oxide Per cent	Stainless steel	Carbon steel
Fe_2O_3	30-60	30-50
ZnO	1-10	10-35
PbO	0.2-2	1-5□
CdO	0-0.1	
Cl + F	1-4	
Cr_2O_3	10-20	0.1-1.0

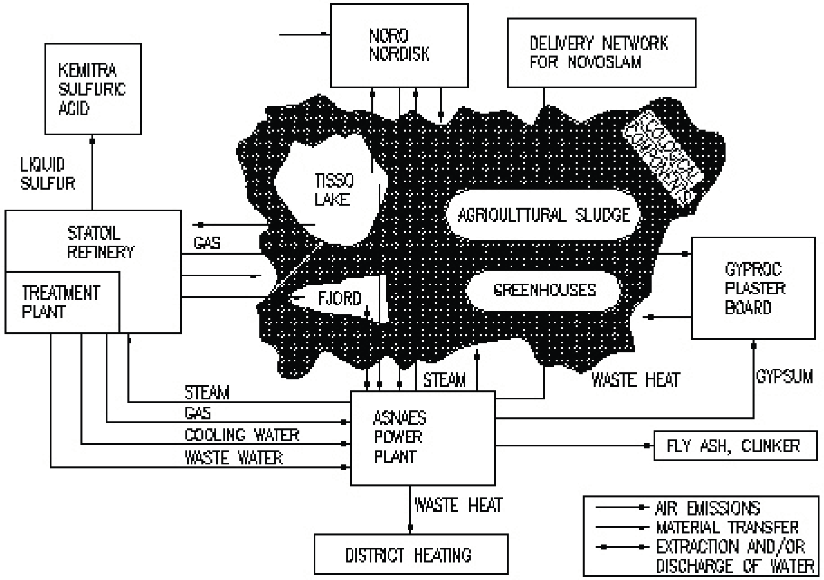

Fig. 19.2. The industrial symbiosis at Kalundborg

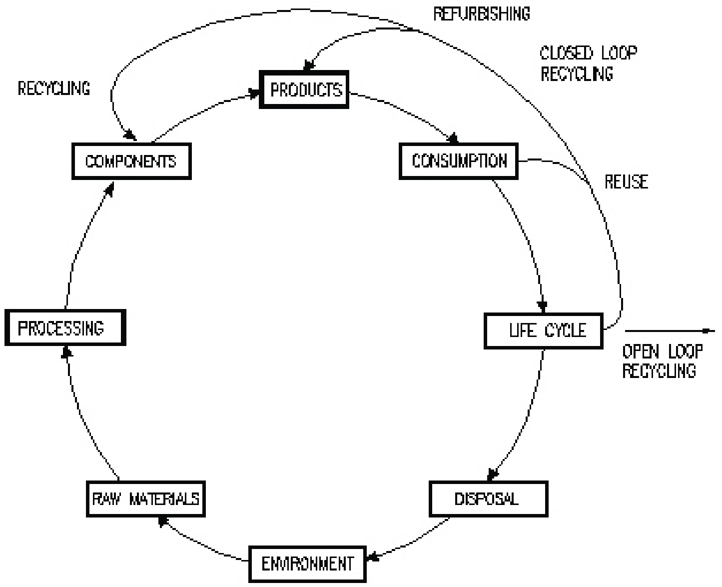

Fig. 19.1. Concept of industrial ecology

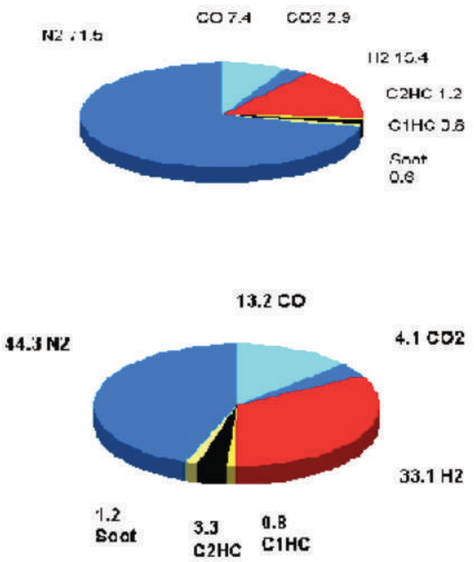

Fig. 19.3. Composition of gas products when organic waste is treated by plasma pyrolysis

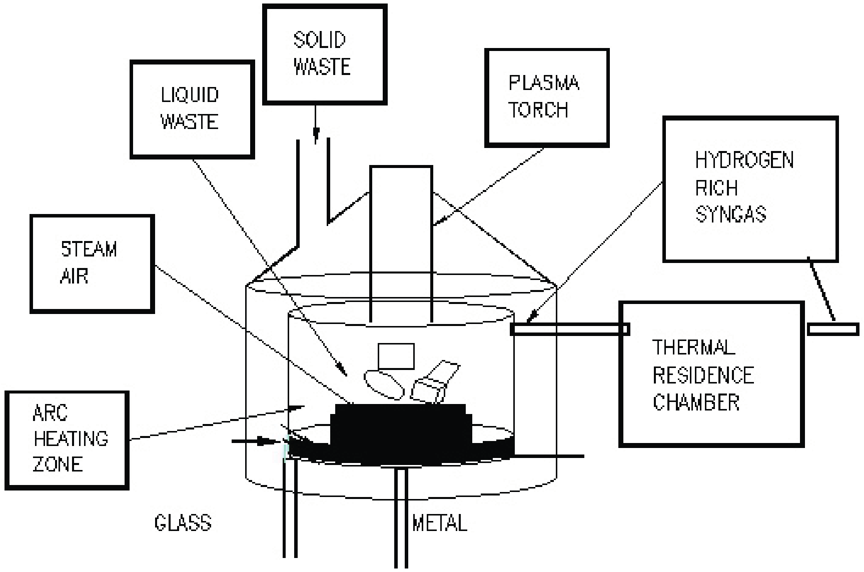

Fig.19.4. Schematic diagram of an energy recovery system using plasma pyrolysis

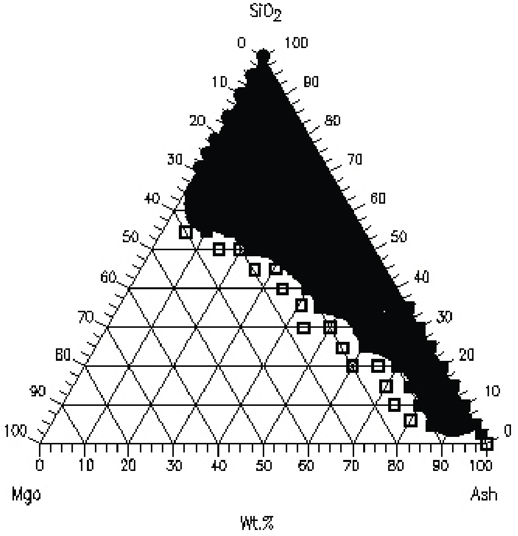

Fig. 19.6. The ternary diagram of glass forming regions

20. A Thousand Suns

Plasma in our Future

The dwindling reserve of fossil fuel is driving the efforts towards developing more sustainable energy sources. Thermonuclear fusion is the ultimate plasma processing method where nuclear reaction between light elements releases energy; the process by which stars burn. The fifty year old search for realising fusion has now entered a phase where workable fusion reactors appear feasible. This chapter discusses the basic concepts of fusion and discusses various approaches to their realisation in the laboratory. Fusion power would be the most precious gift of plasma sciences to humanity.

The Global Energy Crisis

The annual statistical review of world energy published by British Petroleum [BP 2003] makes informative though highly disturbing reading. The known reserves of oil and natural gas will run out in about fifty years time at the present rate of consumption. Coal will last for 200 years. Conventional fission also has resources expected to last for 50 years. Fast Breeder reactors, which convert non-fissile fuels into fissile ones, would stretch this by a large factor, if the technology were in place. Nonconventional energy sources like solar energy, wind, biomass etc are dispersed and expensive.

Moreover, international ramifications of the drying up of fuel reserves are not difficult to imagine. Wars for control of the depleting energy resources will be the order of the day. Many believe that a beginning of this has already happened in Iraq. It is no coincidence that geographical locations of large fuel depository are also places under conflict. With the shortage of oil and gas, prices of will definitely shoot up, making them unaffordable to the poorer nations.

The response of large newly industrializing countries likes India and China is predictable. India has a present per capita annual energy consumption of the order of 400 kWh. To bring it to at least 4000 kWh, a level that brings the Human Development Index (HDI) to a better level of well being [Benka 2002], massive investments in thermal power stations would be inevitable. Despite huge deposits of gas hydrates in the offshore regions [Financial Express], the technology for tapping this is still not mature. The country would turn to its coalmines for stoking the thermal power stations. Imagine the environmental impact due to the CO_2 emissions from these power plants.

Assuming that the world population would rise to 10 billion in the next 50 years [UN 1994], and that the average per capita power consumption is 3 kW, the estimated future energy need is 30 Terrawatt year. What happens in India and China would be replicated in other parts of the world.

Energy from Thermonuclear Fusion

There is, however, cause for optimism that these doomsday predictions need not materialize. Well before 2050, the century old quest to generate power from nuclear fusion would have come to reality.

The quest for starfire had started in a shroud of secrecy as soon as the first hydrogen bomb was exploded in 1952. Prof. Lyman Spitzer at the Princeton University, hearing rumors that Argentina had set up a programme to exploit fusion reactions for energy production, conceived what he called stellarator – names evocative of stars are prevalent in the fusion business – in which hot plasma was to be confined by twisting magnetic field lines. The stellarator plasma had a habit of wandering across the field lines and dissipating its internal heat on the confining walls. The temperature never exceeded a few million degrees, far below what was necessary for fusion.

Scientists in the Soviet Union had been working on the tokamak fusion device, invented by Russian scientists, Igor Tamm and Andrei Sakharov. Tokamak has a tyre shaped vacuum vessel, which is filled with low-pressure mixture of deuterium and tritium [Fig. 20.1]. A magnetic coil wound around the chamber produces a toroidal magnetic field, along the minor axis. The current flowing in the toroidal plasma heats the plasma by ohmic dissipation. This current also produces a poloidal magnetic field that is in azimuthal direction around the minor axis. The combined field lines winds around the minor axis many many times to produce confining magnetic surfaces to which the plasma particles stick.

Much to the chagrin of scientists from US and UK, Lev Artsimovich, director of the Soviet Programme announced in 1968 that the tokamak could routinely produce plasmas at a temperature of 10 million degrees. British scientists went to Moscow and verified this claim using a measurement based on laser light scattered by the hot electrons. The US stellarator was converted into a tokamak and verified the ability of tokamaks to produce fusion-like plasmas.

The Arab oil embargo gave a boost to fusion research. Big machines like the Tokamak Fusion Test React (TFTR) in the US and the European Joint European Torus (JET) [JET 2002] were built. Japan also entered the fusion race by building JT-60. TFTR produced 10.6 MW of fusion power whereas JET produced close to 16 MW. This was indeed proof that the scientific principle of fusion was sound and the confidence in building larger machines to sustain burning plasma rose substantially.

Fusion Reactions

In a fusion reaction two light nuclei combine to form a heavier nucleus and neutrons, and release energy in the form of kinetic energy of the particles. This happens when the fusion fuel attains temperatures high enough for the nuclei to gain enough kinetic energy to overcome the repulsive electrostatic barrier between the nuclei. The reaction rate increases with temperature and hence the name “thermonuclear” fusion. The particles produced in a fusion reaction do not lead to another fusion reaction and hence no runaway chain reaction is possible. The fuel once ignited can sustain the burn by the energetic alpha particles getting trapped in the magnetic field and depositing their energy within the plasma.

The fusion fire has burned in Sun and stars for billions of yeas. However, on earth it is far more difficult to create the conditions required for a self sustaining, power-producing reaction in the case of fusion than in the case of fission. Producing net amounts of power by thermonuclear fusion devices in the laboratory requires temperatures in the range of 100 million degree Kelvin; 10 times higher than those in the core of the sun. To assess how close a fusion plasma is to ignition, the triple product of the number of fuel particles per unit volume n, the time during which the particles retain their energy or confinement time, τ and the temperature, T must be above a threshold value

Several types of thermonuclear fusion reactions are possible between the light nuclei: Hydrogen (H) and its isotopes Deuterium (D) and Tritium (T), an isotope of helium, He^3, Boron (B), and so on. On earth, the easiest reaction to be realised is that between a Deuterium and a Tritium nucleus, because it is the one that occurs at lower temperatures.

In the D-T reaction, a Deuterium and a Tritium nucleus fuse to produce a He^4 nucleus, the alpha particle, with a kinetic energy of 3.5 MeV, and a 14 MeV neutron (because of the conservation of momentum, the kinetic energy of the neutron is four times that of the alpha particle). The alpha particle is positively charged, and hence interacts with the other charged particles in the plasma; the neutron does not interact, and escapes from the plasma region.

The neutrons produced in the D-T reaction carry four fifths of the energy released away from the plasma and hit the stopping region or blanket, where they are slowed down, thereby heating the blanket. Coolants circulating within the blanket transfer the heat out of the reactor area to produce steam and to generate electricity in a conventional way [Fig. 20.2]. The blanket also serves another essential purpose in a D-T reactor: producing, or “breeding”, the tritium fuel required by the reactor.

The D-T reaction is self-sustained when the alpha particles, which carry the remaining fifth of the energy released per reaction, remain confined long enough within the plasma to transfer their kinetic energy to other confined nuclei through collisions – alpha particle heating – thus maintaining the required temperature. This fraction of the energy eventually impinges as radiation and energetic particles on the first solid wall facing the plasma.

In order to achieve ignition in a 50/50 D-T plasma, a temperature between 10 and 20 keV (that is, between around 100 and 200 million degrees centigrade) is needed and the condition on the triple product is:

$n\tau T > 3\ 10^{21}\ m^{-3}$ keV s.

In a reactor, of course, the fusion power output has to be larger than the power spent in maintaining the fusion conditions. The ratio is the reactor gain and has to be many times unity. In an ignited reactor the gain is infinity.

Fuels for Fusion

A kilogram of D-T would release 10^8 kWh of energy (3.39×10^{11} J per gram) and would provide the requirements of a 1GW (electrical) power station for a day. Deuterium occurs naturally in water, while Tritium has to be manufactured. In a reactor, once the initial start-up inventory of previously produced tritium has been used up; tritium can be obtained by neutron bombardment of the element Lithium contained in the blanket, from a fission reaction that also produces helium.

Deuterium and Lithium, the primary fuels for D-T fusion reactors are very abundant on earth. Deuterium is present in all water (one D atom out of 6700 H atoms) and Lithium is widely distributed throughout the earth’s crust at rather low mean concentrations (30 parts per million by weight), with known deposits of Lithium at higher concentrations around the world. Moreover, the concentration of Lithium in the ocean is about 0.2 ppm. Fusion will consume very small quantities of these fuels, 0.5-5 tonnes per GW (e), depending on the efficiency of using the natural lithium. The total reserves of lithium are estimated to be 10^{16} Gigajoule equivalent in land, and 10^{19} Gigajoule equivalent in the sea, sufficient for thirty thousand, and thirty million years respectively, at today's energy consumption rate.

Approaches to Fusion: Magnetic Confinement

It was realised very early that the fusion reactors might be of two types. There are based on the two fundamentally different approaches towards the goal of keeping hot plasmas away from material walls for as long as required by the n□T criterion: magnetic confinement and inertial confinement. The magnetic confinement approach aims to obtain fusion power in low density steady-state plasmas; in this sense, it can be compared with gravitational confinement in the sun, which assures ignition in the core of the stars. The inertial confinement approach aims to obtain fusion energy in a pulsed fashion, from thermonuclear micro-explosions repeated at high rate: it is in fact a development of the principle used in a thermonuclear weapon. The pulsed reactor is like a hydrogen bomb where unconfined high density plasma in a micro-explosion generates all the fusion energy output in a disassembly time. A third version, which is more recent, is a combination of the two, medium density plasmas confined by magnetic field, the so-called magnetised target fusion system. Significant progress towards fusion reactor development has taken place hand in hand with the development of the science of fusion plasmas.

Magnetic confinement fusion (MCF) exploits the ability of a steady magnetic field to dramatically restrain the motion of the plasma charged particles across the magnetic lines of force, while allowing the particles to move freely move along the magnetic lines of force. Certain magnetic field configurations have been developed to keep a low density hot plasma 'levitating' as a whole, far from material walls, in a stable way, and for long times. These are configurations where the magnetic lines of force form globally closed nested surfaces. A large family of MCF devices has been conceptualised. The tokamak is the most developed member of this family, and indeed the device where reactor parameters have been more closely approached.

Magnetically confined plasma in a fusion reactor is fundamentally a system far from thermodynamic equilibrium (unlike the fusion reactor held by gravitational fields in the sun) and is sustained in this state by sources of heat and particles. It has enormous reservoirs of free energy in the form of expansion free energy, free energy of the magnetic fields sustained by plasma currents etc. These free energy sources have the potential to excite collective plasma instabilities, which may impair the performance of the reactor. If the instabilities are gross (with a scale size comparable to the size of the reactor plasma) they can destroy the confining magnetic configuration. Such macroscopic instabilities are to be completely avoided and often restrict the parameter space of operation (such as the plasma current for a given external field, plasma pressure for a given magnetic pressure etc.) of the reactor. Within the allowed parameter space, there may still be microscopic instabilities (or turbulence with scale sizes much less than the plasma radius), which influences the plasma heat confinement.

The Inertial Confinement Approach

The central idea of inertial confinement fusion is to create a transient 'microsun'. If intense beams of radiation or particle beams of short duration irradiate a tiny pellet of fusile material, the thin outer shell of the pellet will absorb all the energy, get heated and fly outwards. The expanding plasma shell can be compared to thousands of tiny jets, each pushing the unheated inner core inwards resulting in its collapse inward. The resulting compression will heat the core to extremely high temperature and a fusion burn would start in the core where fusion reactions occur in great numbers due to the extremely high density of the compressed material. The required compression is at least 1000 times the liquid density and a temperature of 50 million degrees. The whole sequence of events would have to be engineered in a time shorter than the inertial time for the assembly to keep itself together. This process has considerable energy gain, because the amount of energy needed to ignite a hot spot is small compared with the fusion energy released. The burning of this colder fuel must take place during the small time interval over which the pellet keeps together: in this case, confinement relies exclusively on mass inertia, hence the name "inertial confinement" [Fig. 20.3]. For ICF, the ultimate goal for energy production would be to repeat such single micro-explosions of pellets of mass of a few milligrams at a rate of about 10 explosions per second with a Q factor of 50 to 100.

The idea of using intense laser pulses to initiate inertial fusion was first proposed by Basov and Krokhin [Basov 1964]. Ignition and breakeven using this approach is expected to need a laser energy of about 1 Mega Joule. There are a number of other issues, which have to be solved before success with inertial fusion is achieved. The deposition of energy in the outer shell produces energetic electrons, which propagate into the core and pre-heat the fuel. This problem has been solved by clever pellet design and using short wavelength lasers. The pellet has to be illuminated uniformly to avoid hydrodynamic instabilities from creating an asymmetric implosion. In addition to using a large number of beamlets to do the implosion, optical smoothing techniques have been developed. Another solution around this problem is to convert the driver laser energy into x-rays first by making them fall on the inner walls of a cavity surrounding the pellet and use the x-ray flux for compression. In the fast ignition concept, DT fuel is compressed to a density of 300 grams/cc followed by irradiation with a 20 picosecond "fast ignition" pulse of laser energy or fast ions, which generates MeV electrons that heat the DT fuel to 10 keV. Fast ignition can provide more target gain and a lower input threshold energy than the direct (single stage) or indirect drive proposed for the National Ignition Facility (NIF). Recent fast ignition experiments have shown a 20% energy transfer from the laser to the imploded plasma.

Large laser facilities have been built in the United States, France and Japan where these ideas are pursued with considerable vigour. The National Ignition Facility (NIF), currently under construction at the University of California's Lawrence Livermore National Laboratory, is a stadium-sized facility containing a 192-beam, 1.8-Megajoule, 500-Terawatt, 351-nm laser system together with a 10-meter diameter target chamber with nearly 100 experimental diagnostics; scheduled for completion in 2008. NIF is being built by the National Nuclear Security Administration and when completed will be the world's largest laser experimental system, providing a national centre to study inertial confinement fusion and the physics of matter at extreme energy densities and pressures. NIF's 192 laser beams will compress fusion targets to conditions where they will ignite and burn, liberating more energy than required to initiate the fusion reactions. NIF experiments will allow the study of physical processes at temperatures approaching 100 million K and 100 billion times atmospheric pressure.

The French "Laser Megajoule" (LMJ) is designed to deliver on target 1.8 MJ and 550 TW of 350 nm UV-light. Operation should start in 2009, and the system should be able to deliver 600 shots per year. The construction of the building has begun recently and will take about 4 years. The target chamber will be 10 m in diameter and a (cryogenic) high precision target holder is being developed. A prototype experiment ("Ligne d'Integration Laser", LIL) consists of a group of 8 laser beam lines (out of 240 for LMJ) and a 4 meter diameter target chamber. First results have been obtained on one beamline of LIL with pulses of 18 kJ at 1053 nm and 7 kJ of UV, shaped as a 20 ns prepulse followed by a 3 ns main pulse, in accordance with expectations.

An ICF reactor is a driven reactor by nature, so the ignition criterion used above can only be used to gain an idea of the magnitudes involved. For ICF, fuel has to be compressed at densities up to about 1000 times liquid density for n□T to approach ignition values: this is because □ is predetermined by the size of the pellet, as the time the fuel keeps together is roughly the radius of the pellet divided by the burn wave sound speed. This time is of the order of 100 picosec, and accordingly, the densities in ICF are around 10^{10} times higher than in MCF.

The Tokamak Reactor Technology

The front-running fusion device is the tokamak. The name is a contraction of the Russian words for "toroidal," "chamber," and "magnetic." Early tokamaks were conceptually simple devices; it is a transformer where the primary coil is excited to produce currents in the secondary, which is a conducting plasma loop. Over 100 hundred tokamaks, big and small operating in laboratories around the world have been the study tool to understand the behaviour of high temperature plasmas held in confinement by magnetic field. The conventional tokamak combines magnetic fields generated by magnetic coils encircling the donut-shaped device with electric currents flowing within the plasma to create a magnetic field configuration that confines high temperature plasma. Transformer action is based on changing the magnetic flux in the core of the transformer, and since only a limited flux can be stored in the core, these devices are pulsed. It means that the tokamak plasma is transient, existing typically for a few seconds.

The first transformation of the early tokamaks to the modern fusion-worthy devices was to make the tokamak a steady state one. Fortuitously for hot plasmas confined in toroidal magnetic field, the radial pressure gradient and the plasma flow combine to create a self-driven (bootstrap) current. It is estimated that upto 80% of the plasma current can be driven this way. Additional methods have to be found to drive currents in the plasma without using the transformer action. Fortunately, many ways have been found to do this. The most efficient way is to push the electrons in one direction, thereby driving a current, using the momentum imparted by radiofrequency waves. The required RF power for a reactor is of the order of 100 MW.

The reactor plasma will be heated to the fusion burn conditions by injecting intense beams of high energy neutral particles. Neutral beams are unaffected by the confining magnetic field and can move through it to the core of the plasma where they will be ionised and trapped and their energy stripped by the plasma particles colliding with them. However, to reach the core before being ionised in the outer parts they have move with high speeds. The required beam energy is in the range of 100-200 keV. The power contained in the beam also must in tens of MW.

Auxiliary power from radiofrequency or microwaves can be deposited into the plasma to heat it to the required fusion temperature. The injected wave can resonantly interact with the characteristic waves within the plasma and transfer energy. These waves exist at the multiples of the characteristic electron and ion cyclotron frequencies as well as their hybrid combinations.

Tokamak reactor will use superconducting magnetic coils since the energy consumed by resistive magnets would be too large. Fusion magnets are very large with many meters in diameter. Since the fusion plasma has D-shaped cross section known to be able to contain higher plasma pressures than circular plasma, the magnetic coils also will have non-circular in cross section. Reactor magnetic coils are designed to produce magnetic fields upto 14 Tesla (500,000 times the magnetic field of the earth).

For the fusion plasma to burn continuously, it must be fuelled to replace the DT fuel atoms spent in the fusion process. Fuel is added by shooting pellets of deuterium ice into the plasma core. To take the fuel to the core of the hot plasma, the pellets have to be shot with high speeds; upto 2 km/sec using high-pressure gas gun propulsion. The Helium ash created in the fusion reaction has to be continuously exhausted. Helium as well as impurities are removed from the hot plasma by opening up the toroidal magnetic field lines at the edge and diverted into a scavenging chamber and the particles are scraped off.

The neutrons produced in the fusion reactions fly off towards the walls, since they are not confined by the magnetic field. They are trapped in ‘blankets’ which moderate and capture the neutrons, converting their kinetic energy to heat, which can be used to produce steam to drive the reactor turbines. The blanket also breeds the Tritium fuel from Lithium through the reactions:

$^{6}Li + n = T + {}^{4}He$

$^{7}Li + n = T + {}^{4}He + n$

Fusion research can now boast of many successes. Research devices have reached temperature of 100 million degrees by using magnetic fields to confine the plasma. Researchers have now produced fusion power up to 16 M W. The steady progress in the performance of tokamaks [Fig.20.4] has been quite impressive. Another important empirical discovery is that the performance of all the tokamaks depends on a scaling law, which can be used to predict the performance of future machines [Fig. 20.5]. The challenge is to make fusion energy economical, environmentally practical, reliable and safe.

Material issues are critical for the development of fusion reactors [Ehrlich 1999]. The structural materials used for vacuum vessels etc. would be subjected to a steady fusillade of energetic neutrons. Each atom may be displaced up to 30 times in a year of operation. New alloys like EUROFER in which alloying elements with a high probability for neutron activation are replaced by more benign materials like Tungsten, Tantalum and Vanadium. The Chromium content is optimised to be corrosion resistant under neutron irradiation conditions. Research on Vanadium alloys and ceramic composite materials based on silicon carbide are in progress.

It is estimated that in a fusion reactor, 20 per cent of the fusion energy would be deposited on the surface of the components most proximate to the plasma, the so-called plasma facing components (PFC). The surfaces on which the diverted plasma flow would terminate will experience local heat loads of the order of 10 MW/m^2. Carbon fibre reinforced carbon composites are expected to withstand such thermal loads.

To develop and test these materials, experimental facilities, which will produce neutron fluxes comparable to actual fusion reactors, have to available. Such a facility based on accelerator produced neutrons; International Fusion Materials Irradiation Facility (IFMIF) is being planned under the auspices of International Energy Agency [Kondo 1998].

Prospects for Fusion Reactors

When will fusion power light up homes?

The fortunes of fusion have waxed and waned in tune with oil prices and international political turmoil. Some analysts find a direct correlation between political events and the steps in advancing fusion [Conn 1999]. From the time fusion research became declassified in 1958, there has been remarkable co-operation in fusion research at an international level. Even at the worst of times in US-Soviet relations, the collaboration continued through the development of the INTOR concept of a large next generation tokamak in 1978 under the auspices of the International Atomic Energy Agency (IAEA). With the end of the cold war and following the Reagan-Gorbachev summit in Geneva in 1985, the idea of an international fusion project, to be built by the then Soviet Union, the United States, Europe and Japan was nucleated. The Conceptual Design Activity for the International Thermonuclear Experimental Reactor (ITER) began in 1988 under the auspices of

IAEA and was completed in 1990 [ITER 2002]. The financial constrains demanded a reduced cost approach and resulted in the ITER-FEAT (Fusion Energy Amplifier Tokamak). Engineering Design Activity commenced in 1992 and finished in 1998 [ITER 2001]. The total construction cost is now proposed at over $5 Billion with at least a $500 million dollar per year operating cost.

The way to ITER (by an odd coincidence Iter means the way in Latin) has had its ups and downs. The high cost of the early design made US exit the international collaboration. With more realistic design and cost US rejoined the effort in 2003. China and Korea also have become partners in building the device. Construction of ITER is expected to begin in 2003 and the machine will be ready by 2013 [Fig. 20.6]. After the initial trials, the machine will start experiments with DT fuels and is expected to produce 500 MW of fusion power for 500 seconds in each experiment run. Successful test of ITER is expected to pave the way for building the ‘demo’ reactor in 2030 and finally a fusion power plant by 2050. Designs for Fusion reactors already exist; ARIES-AT in the US [Conn 1990] and the Steady State Tokamak Reactor (SSTR) in Japan [Seki 1991] are contending concepts for a fusion power plant for 1000 MW electrical output.

Estimation of the actual price of power from fusion reactors is beset with many uncertainties related to optimization of physics of the device, development of reliable materials and power plant operating scenarios and acceptable levels of safety and environmental performance. The general consensus is that with the current levels of physics and material technology inputs fusion power would be costlier than power from fossil fuels but would be comparable to power from alternative energy sources, with the added bonus that the power supply would be reliable. A typical breakdown of cost is 40% from fusion specific capital, 40 per cent from operation and consumables and 20% from non-fusion specific plant. With improvements in materials and physics the power cost could approach the fossil power prices [Hender 1996]. Estimates put the cost of electricity to consumers from such an advanced tokamak at 70-130 mECU/ kWh, which is comparable to that of electricity produced by today’s fossil fuel and nuclear plants. Electricity produced in advanced tokamaks should be competitive in future energy markets.

Non-electric Applications of Fusion

Are fusion devices limited to only producing electricity? A growing group of plasma physicists are looking at novel and inventive applications of the heat, radiation and particle flux from fusion devices for near term non-electric applications. The argument is that much before power producing fusion reactors are built, sub-critical fusion devices could yield commercially attractive products and applications.

The most attractive and commercially viable applications exploit the energetic neutrons from fusion reactions [Kulcinski 1998]. The annual demand for radioactive isotopes for medical, industrial and research applications, worth approximately 100 million US dollars, could be substantially met from small fusion devices. Cobalt ^{60} is a radioactive material which can be produced in such reactions and which have extensive use in sterilization of medical products and food as well in cancer therapy. Portable neutron producers for detecting contraband explosives using nuclear techniques are another area of interest.

Destruction of hazardous waste and ‘burning’ of nuclear waste by transmutation reactions [EPRI 1997] are other potential applications. Radioactive waste materials are toxic and carcinogenic. The wastes are typically ^{235}U, Plutonium isotopes, and actinides like Neptunium, Americium and Curium. Even after several hundred years of cooling the decay heat is considered to be an agent in triggering the release of the nuclear material from deep geological disposal sites to the biological environment. Small compact volumetric neutron sources based on 70-250 MW level reactors based on spherical torus could be exploited for these applications [Cheng 1998]. The steady state Inertial Electrostatic Confinement (IEC) devices [Hirsch 1997] producing 10^{10} neutrons per second and costing les than $ 100,000 appear to be promising. Higher neutron fluxes may be available from alternate fusion concepts such as Field reversed configuration (FRC), and Spherical Torus (ST), which could not compete with tokamaks in the fusion race.

The high energy neutrons also can be effectively used for radiography where the traditional x-ray based technique fail because of their inability to penetrate thick or heavy metals. Another technique related to radiography is thermal neutron activation where the nitrogen contained in most explosives are activated and made to emit signature gamma rays. This is now considered a timely diagnostic to detect contraband explosives.

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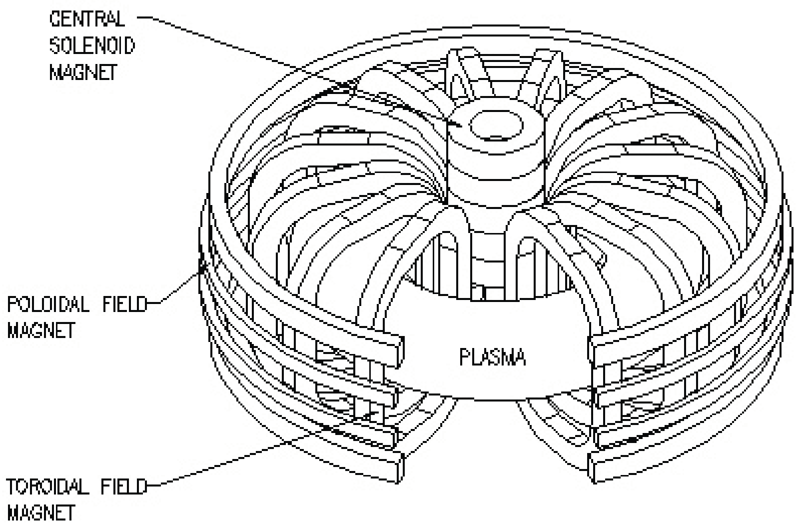

Fig. 20.1. Schematic diagram of the Tokamak device

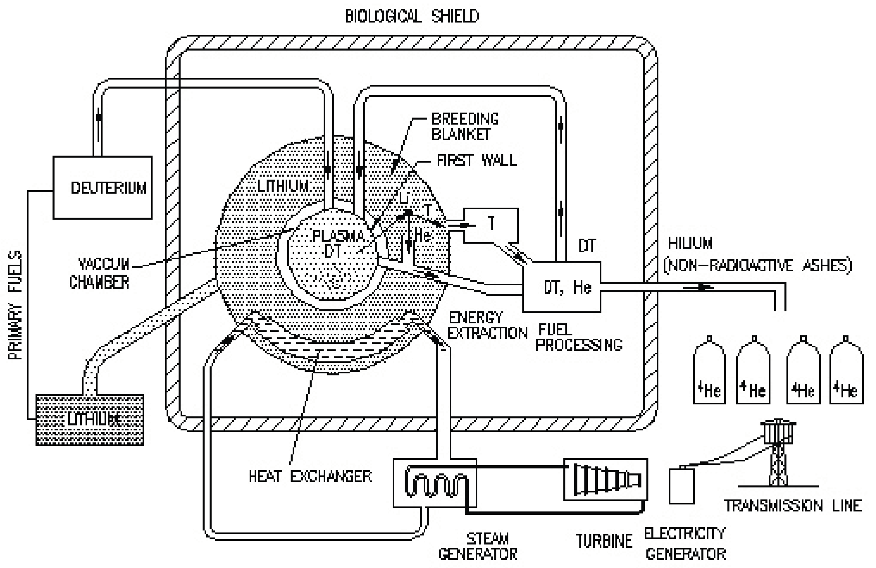

Fig. 20.2. Basic concept of a power producing thermonuclear fusion reactor (figure courtesy, IAEA, Vienna)

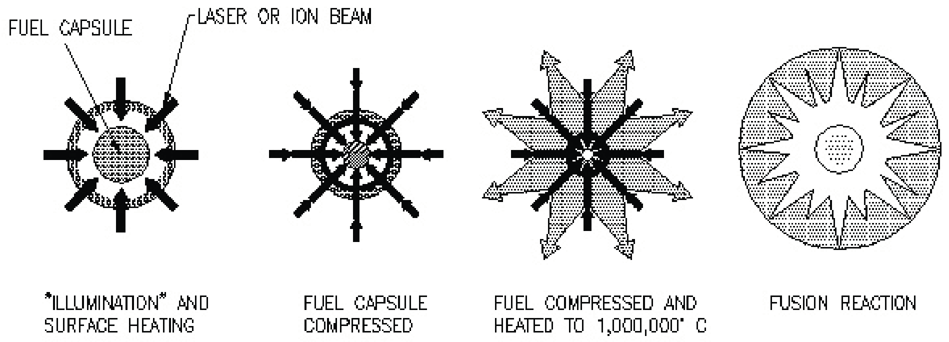

Fig. 20.3. Schematic diagram of laser fusion

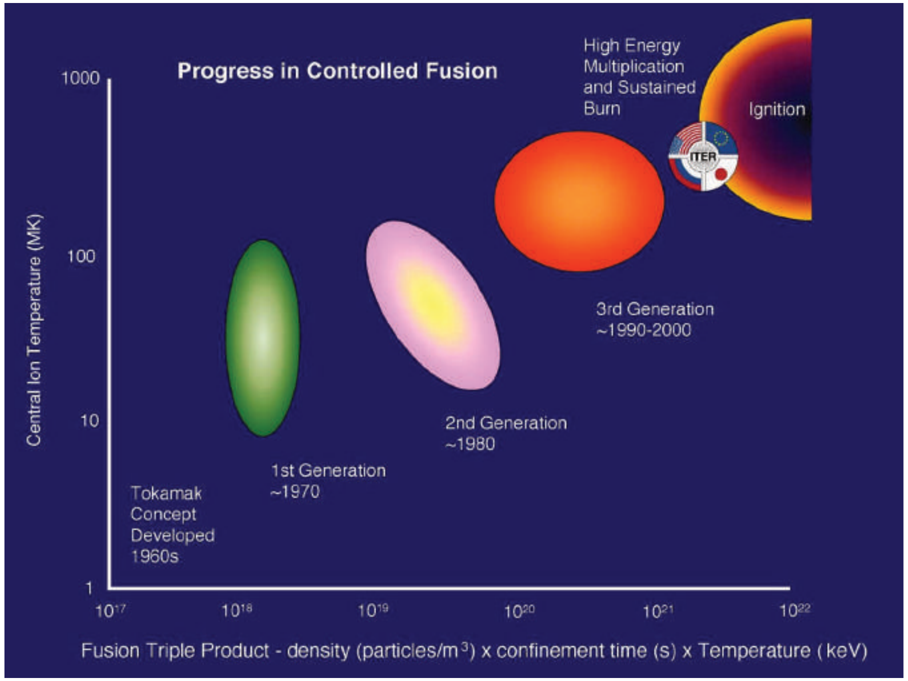

Fig. 20.4. Progress in the performance of tokamaks over the years (courtesy ITER)

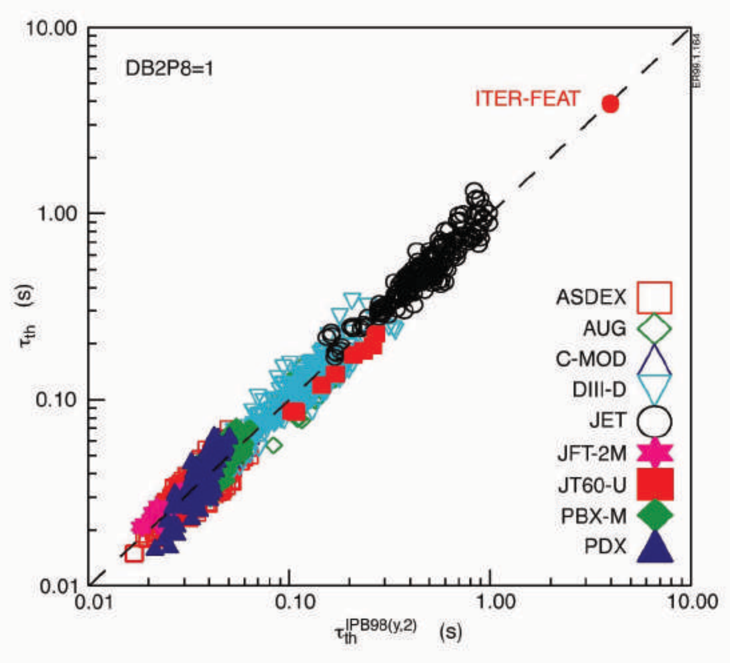

Fig. 20.5. The 'ITER' scaling law for tokamak fusion devices (courtesy ITER)

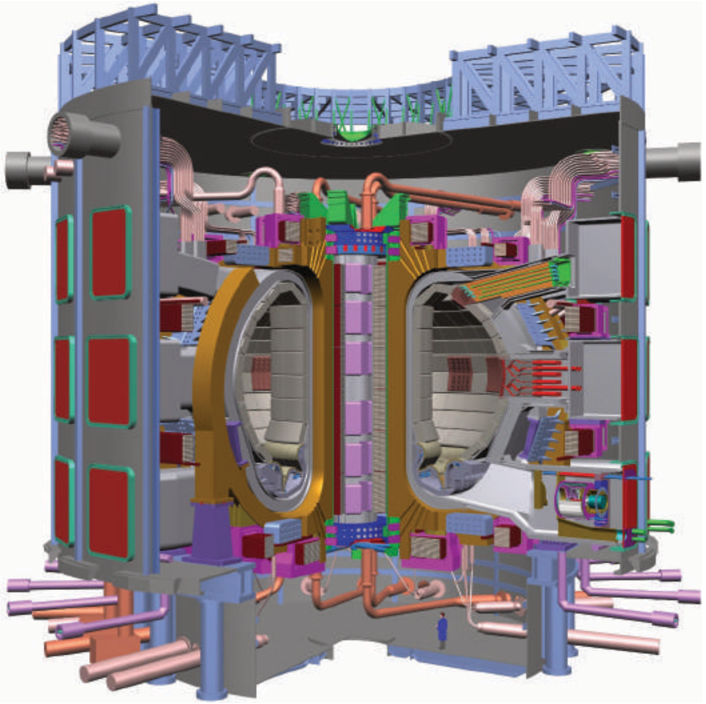

Fig. 20.6. An artist's view of the ITER tokamak (courtesy ITER)