1. Introduction

Plasmas and their products are ever present in modern life. Over one billion fluorescent lamps are fabricated each year. World-wide annual sales of semiconductor devices total over $12 billion. Metallic components are hardened in plasmas in over 1000 industrial sites to improve their wear and corrosion resistance so providing more reliable parts for all types of machinery, including cars and aircraft. These processes and products are all reliant on the use of plasmas. They represent some of the relatively mature applications of plasma-based processing but there are now many other applications under development. Some, already into the production phase are the extension of micron-scale engineering to information storage, display technology, micro machine fabrication. Still developing is the use of plasmas to modify the surfaces of soft materials such as polymers, textiles, and even biological materials, and so change their functionality. Improving existing processes and products and developing and implementing new applications requires a basic understanding of the plasma environment and its interaction with surfaces.

This first part of this article will be a general ove rview of plasma applications. Many of the applications will be listed, with a few described briefly. In following weeks common themes will be developed.This cource dealt with phenomena in plasmas produced in atomic gases such argon. It will emerge here that in most applications the plasmas are created in molecular gases and, more often than not, gas mixtures. So we will extend the discussion of plasmas to these more technologically relevant systems i.e. those created in molecular gases.

It will also emerge that many processes involve the interaction of the plasma with material with which it is in contact. So an account of plasma surface interactions, including the basic concepts of surface physics is required to understand what happens when ions, electrons, photons and chemically active radicals are incident on a surface immersed in a plasma. This background knowledge will enable you to understand in detail a treatment of surface processing applications e.g. surface activation, sputtering, etching, deposition and implantation and specific applications.

1.1 Plasma applications.

Plasmas are produced by coupling energy into a material which can be initially in a solid, liquid or gaseous form. In application this is generally through injecting electric power or laser power. The former being by far the most common and is the method exclusively discussed here. It is convenient when discussing the applications of electrically-produced plasmas to divide them up into three broad categories. You will see the word generally appearing frequently in this section. This categorisation is a generalisation and many processes work at the interface or beyond these classifications.

1.1.1 Low pressure, high temperature plasmas.

Although this is outside the remit of this course it is worth noting that one of the most potentially significant contributions that plasmas may make to human-kind is in controlled nuclear fusion. This represents the potential to produce energy for many millennia by creating the conditions under which light nuclei, such as the deuterium isotopes of hydrogen, fuse together to form heavier nuclei with an associated release of energy.

This requires the heating of deuterium plasma with a density of 2-3 x 10^{20} particles m^{-3} to temperatures in excess of 100-200 million K for a period of one or two seconds. The containment exploits the fact that at these temperatures the gas will be in the plasma state and the charge particles will therefore respond to magnetic fields. Careful design, such as that of the Tokomak, holds the promise that this difficult task can be achieved. These are very expensive devices and an $9,000 M dollar next step towards a power generating nuclear fusion device has been designed and will soon be constructed, once the politicians can decide between France and Japan for its final location.
The scientific issues are somewhat different from those that are the focus of this course. However at the edge of these devices there exist conditions, such as a cooler plasma in contact with surfaces, that are not dissimilar to those encountered in many commercial plasma systems.

For more information see www.jet.efda.org/pages/fusion-basics.html and www.iter.org

1.1.2 Thermal plasmas

Thermal plasmas are normally created at close to atmospheric pressure. The high power input required to sustain the discharge and short time between collisions mean that all the components of the plasma (i.e. electrons, ions and neutral atoms/molecules) have similar temperatures generally in the region of 1,000 to 10,000 K. A significant fraction of the gas is ionised.

They have been used mainly, but not exclusively to deliver heat to a surface to

- increase surface reactions
- produce melting
- sintering
- evaporation

and find applications in

- welding
- metal recovery

- waste treatment
- plasma spraying
- arc lighting
- plasma scalphels
- ozone production
- electrical switches

1.1.3 Non-thermal plasmas

Non-thermal plasmas generally operate at low gas pressures i.e. markedly less than atmospheric. The lower collisionality and power input means that the plasma components have widely differing temperatures with electron temperatures ranging from 10,000 to 50,000 K while the ions, neutral constituents are at about a 100's K. Only a small fraction (10^{-3} to 10^{-5}) of the gas is ionised.

These are generally used in lighting and the chemical or physical modification of surfaces with applications in

Lighting	
Displays	
Gas lasers	
Etching	microelectronics micromachines
Deposition	microelectronics diamond film growth decorative coatings optical coatings biocompatible coatings
Surface Modification	surface hardening of metals plastic and textiles water resistance and wettability
Ion sources	accelerators, including implanters ion thrusters for space craft
Medical Applications	plastic and textile changes to influence cell growth sterilisation

1.2 Specific applications

Below a few of the applications of plasmas to products and processes are briefly discussed. These have been chosen to give some idea of the breadth of plasma applications and also to draw out some common themes for further study. There will be more detailed of some of these and other processes towards the end of the course.

1.2.1 Lighting

The most significant industrial application of plasma systems is in the lighting industry. The normal fluorescent tube consists of a plasma produce containing Mercury (1 Pa partial pressure) and Argon (400 Pa partial pressure). They convert electricity to light at an electrical efficiency of between 25 to 30 % i.e. substantially more efficiently than incandescent (filament) light bulbs. UV light is produced by the decay of excited mercury in the discharge tube and is converted to "white" light by a thin film of phosphor material on the walls of the tube. Since lighting consumes about 1,000 billion kWh per annum, about 10-15% of global energy production and up to 35% of the energy production in some less developed countries, there is constant development of plasma-based lighting systems. This work seeks not only to improve their efficiency but also their colour quality and to remove the need for mercury and phosphors. The most modern high-pressure mercury lamps are metal halide lamps which use sodium, thallium or indium iodide to affect such improvements and require no phosphor.

1.2.2 Lasers

The earliest laser was a ruby laser announced in 1960. The population inversion and lasing action in this device take place in a doped crystal, but here it is worth pointing out that the crystal is energized externally by means of a plasma flash lamp. In 1961 a new type of laser, a He-Ne gas discharge laser, made its debut and gas lasers have dominated industrial applications ever since. While low power solid-state lasers have now become widely available, they are not suitable for medium to high power applications.

A range of different species in the plasma are involved in lasing. Neutral neon atoms emit the characteristic red laser light of the He-Ne laser. This laser consists of an electrical discharge in a gas mixture of 10 parts He to 1 part Ne, sitting in an optical cavity. Lasing requires that there are more atoms excited into some high lying states than into lower lying states. This is called population inversion since in thermal equilibrium the number of atoms in excited states would decrease exponentially as the energy of the states increase. In a He-Ne plasma population inversion is achieved because of collisional transfer of energy from (long-lived) metastable helium levels to ground state neon atoms, exciting them to those specific high lying states. The metastable He is created in collisions with energetic plasma electrons. Population inversion allows the process of simulated emission to take occur at a high rate. The optical cavity is formed by two highly reflecting mirrors are placed at each end of the discharge tube with a separation tuned to the wavelength of the stimulated emission so it bounces back and forward in the cavity, stimulating more emission and so amplifying the light intensity. The unique high directionality, narrow bandwidth and high coherence of this LASER light stems from this Light Amplification by Stimulated Emission of Radiation.

Other gas lasers include those produced by discharges in the vapour of metals such as copper. The emitting species is an ion rather than an atom in e.g. the green or blue emitting argon ion lasers.

Another class of lasers uses molecules excited into different vibrational rather than electronic, energy levels to achieve laser action. The most common is the high power, up to gigawatts in pulsed mode, CO_2 laser which operates in a range of wavelengths in the infrared. It is the most widely industrial laser with applications in cutting, welding and even as a surgical tool. There are many other molecular lasers were careful tailoring of the discharge and wall conditions allow the full molecule to stay intact rather than dissociate or that create the lasing species in the plasma volume e.g. HCN, ArF* and KrF* lasers. These latter excited dimers, or eximers can exist in the plasma state but would dissociate spontaneously in their ground state.

1.2.3 Plasma displays

Plasma displays consist of arrays of small discharges (about 100 x 300 x 1,000 μm^3). A group of three of discharges constitute one pixel, one producing red, one green and one blue light. A 60 inch plasma screen consists of an array of 1366 x 768 pixels i.e. 4098 x 768 discharge cells. The discharges are struck typically in a 10% Xe and 90% Ne gas mixture typically at a pressure of about 70Pa and driven by a 200 V voltage, modulated at 100 kHz. The plasma produces VUV radiation from excited Xe and Xe_2. This is converted to red, green or blue radiation depending on the phosphor on the viewing surface of that particular discharge cell. The back face contains the electronics to fire the appropriate discharges to create the required pattern or image. Clearly issues such as the turn on and off times and the refreshment time for the discharge are critical.

1.2.4 Plasma etching

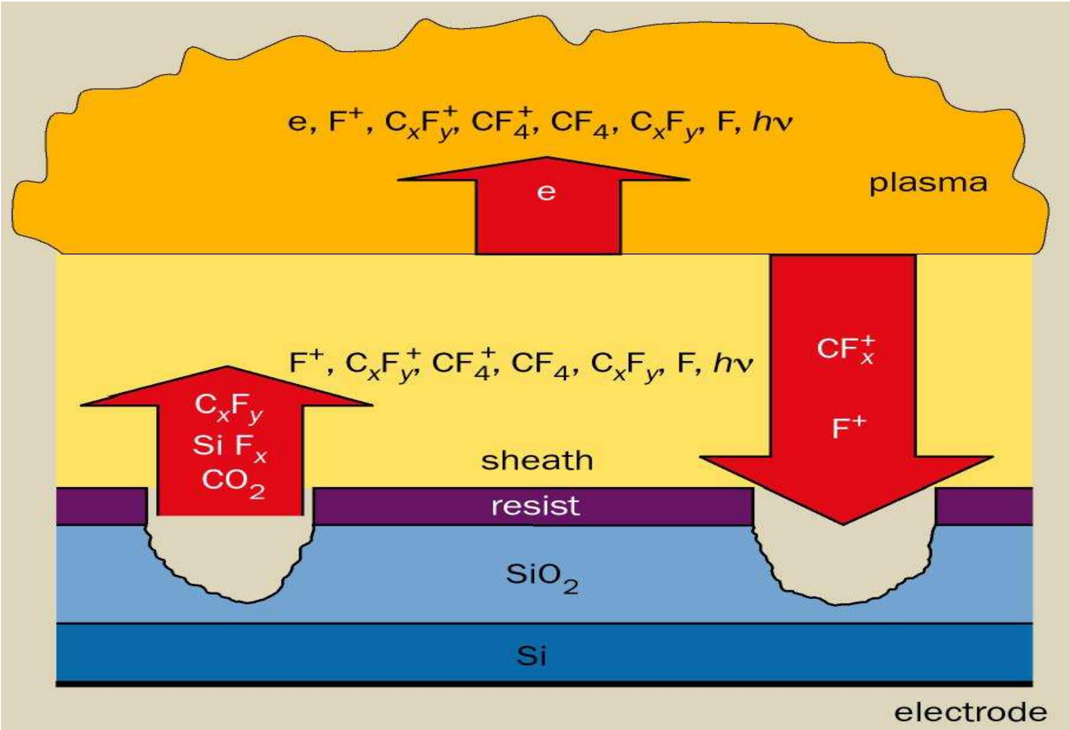
Probably the most sophisticated applications of plasmas are to be found in the microelectronics industry. There the creation of architectures of semiconducting, insulating and metallic materials by the addition (deposition) and subtraction (etching) of many layers of different materials produces some of the greatest challenges. The current devices incorporate feature sizes as small as 130 nm, with the pursuit of ever faster devices pushing this specification to 100 nm by 2005. Of the hundreds of processes used in the fabrication of a state-of-the-art microchip about one third involve the use of plasma for etching, deposition, cleaning or passivation. It is estimated that about 60% of the $2 billion required to set up a fabrication plant for the next generation of microchips will be the cost of plasma processing-related equipment.

Critical specifications are the etching and deposition rates, their uniformity over the wafer surface and their reproducibility from wafer to wafer, the anisotropy of etched patterns i.e. vertical walls on edges of features and in trenches and selectivity between the etching rate of underlying or overlying material. Additionally there is the drive towards ever larger diameter wafers and the introduction of new materials to speed up devices.

This is a vast area and here we will focus on etching. A range of plasma chambers, plasma excitation mechanisms and operating conditions are used, depending on the specific application. Gas pressures used range from 0. 1 to 70 Pa, with electron densities from 10^{14} to 10^{17} m^{-3} and ionization ratios ranging from 1 in 10^3 to 1 in 10^5 , so neutral gas predominates. Importantly the plasma constituents (electrons, ions and neutrals) are not in thermal equilibrium with one another. The input energy is much more efficiently transferred to electrons and since the energy transfer from electrons to ions and atoms in the binary collisions at these low pressures is small, because of the large difference in their masses. The electron temperature (~ 3 eV or about 30,000 K)) is therefore very much greater than the ion temperature which is about 2 to 3 times higher than the gas temperature which in turn is about 1.5 times higher than that of the wafer (~ 300 K). In addition the ion energy to the processing material can be controlled by self biasing of the wafer-holding electrode.

The recipes and chemistries used by plasma equipment manufacturers are process specific, often complex and often commercially sensitive. For them all a critical plasma feature is the dissociation of the molecular gases, generally through collisions with energetic electrons, to produce, from the relatively inert working gases, highly reactive species such as atomic oxygen, hydrogen or completely or partially dissociated fluorine, bromine or chlorine containing molecules. The gas dissociation ranges from ~0.01 to 0.2 of the total gas content.

A simple example, which illustrates the ingenious use of both the chemical and physical aspects of the plasma, is the etching of a feature in an insulating SiO_2 layer which stops at an underlying Si wafer. This is currently one of the largest single etching applications in the microelectronics industry. The process is illustrated in Figure 1.



A fluorocarbon gas is generally used, the simplest being CF_4. In the plasma the gas molecule is dissociated to produce F atoms and carbon-containing radicals. On a Si surface the F atoms do the etching since they combine with the surface Si atoms to form volatile compounds which drift from the surface and are subsequently pumped away. On the other hand the carbon-containing radicals form a polymer which remains on the surface and inhibits the F etching of the surface. The bombardment of the surface by plasma ions, accelerated across the plasma sheath, promotes the removal of both polymer and fluorinated silicon species from the surface. Control of the ion energy is important since if it should be high enough to effectively remove surface products but not so high as to cause damage to layers or structures underlying the surface.

The final etch rate depends on the balance of F and C atoms on the surface which in turn depends on the density of the different neutral species in the plasma, the ion flux bombarding the surface and the ion energy.

On exposed SiO_2 the combination of oxygen and ion bombardment results in the formation of volatile CO rather than a polymer and thus allowing F access to the surface. At low gas pressures, when the ion mean free path between collisions with gas atoms is longer than the sheath width, the ions move along the electric field lines and so strike the surface perpendicularly. This results in highly directional energy deposition producing vertical wall on the etch features, allowing closer packing of the features. In addition polymer builds up on the sidewalls of the feature and since this is not subject to ion bombardment it remains in place so preventing sidewall etching and hence further promoting the anisotropic etch.

Once the Si wafer is reached the polymer also builds up at the bottom of the trench since there is now no O_2 present. This inhibits etching of the Si. Since the ion and atom densities in the plasma may not be uniform over the entire 300 mm diameter of a wafer, the SiO_2 may be etched faster in one region of the wafer than another. The polymer passivation allows the etching process to be run a little longer to ensure that the SiO_2 etch is complete across the whole wafer without etching of the underlying Si. The polymer can subsequently be removed by exposure to an oxygen plasma.

It is clearly essential to get the correct F:C ratio and this can be controlled. For example, in a particular plasma source CF_4 may produce too many F atoms and side etching may occur because there is too little carbon in which case hydrogen may be added to mop up the excess F as HF. Alternatively the same end can be meet by using compounds with lower F:C ratios such as C_2F_4.

1.2.5 Plasma Deposition

Much deposition, particularly of metals, is carried out by using energetic ion bombardment to remove material from one electrode and deposit on the wafer sited opposite it in the discharge. Argon is often used as the processing gas but by adding, for example, nitrogen to the discharge the metal nitride can be deposited.

Interesting synergistic physical and chemical phenomena can also be seen in plasma deposition of diamond coatings where small concentrations of hydrocarbons (e.g. methane or acetylene) are added to hydrogen plasma. The plasma produced hydrocarbon radicals are deposited on the surface and the carbon forms predominantly in the graphite phase but a small quantity of carbon deposits in the diamond phase. The plasma-produced atomic hydrogen efficiently etches the graphite but not the diamond so, over time and with the right hydrocarbon/atomic hydrogen mix, a diamond layer grows on the surface. Such films have many applications including as hard wearing, biocompatible coatings on medical implants.

1.2.6 Polymer and Textile processing

It has been found that exposing polymer and even textile material, such as cotton, to weak plasmas operating in nitrogen or oxygen gas can change the surface functionality. The materials become more hydrophilic i.e. they absorb water more readily. The effect is seen to be permanent and clearly has applications in dyeing and diapers etc! Microscopic inspection of the surfaces, demonstrate that the elemental composition and the nature of the bonding has been changed following the plasma exposure. Exposure to fluorine-containing plasmas can create a similar but opposite effect making the material more hydrophobic i.e. water repellent. Early research indicates that these effects may be produced by a synergy of plasma chemistry, ion impact and even light.

These effects were first explored in low pressure discharges such as those used in the microelectronics industry but operated a very low power. A major recent development has been the replication of similar effects but at atmospheric pressure, but with added helium to allow plasma creation at low powers. This creates a non-thermal plasma at high pressure and opens up the possibility of plasma treatment of materials in the continuous web environment used in the textile and polymer industry.

1.2.7 Ozone production

Siemens developed the first process for the production of ozone in an air discharge at atmospheric pressure in 1857, and ozone was used on a large scale for the treatment of drinking water from around 1900. This is still important today and continuing development is assured by new uses for ozone, such as the bleaching of pulp for paper manufacture which is now replacing the more noxious chlorine bleaching. What seems initially a relatively straightforward process hides considerable chemical complexity involving plasma produced species such as excited molecules, molecular ions and negative ions.

1.3 Conclusion

There are concepts that are important to understand these plasma applications.

They are

- Plasma generation and the production of energetic ions.
- The emission of light from plasmas.
- The production of reactive species from a chemically inert feedstock gas.
- The reactions between the particles produced in the plasma with one another and with the neutral gas and its products.
- The interaction of ions, electrons, photons and radicals with surface in contact with the plasma.

In order to understand the current applications of plasma applications and anticipate new applications it is essential to understand these basic processes. In this course we will look in detail at these issues before eventually returning for a more detailed look some of these and other plasma applications.