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## CHAPTER 3

# COATINGS AND SURFACE MODIFICATION USING LOW PRESSURE NON-EQUILIBRIUM PLASMAS

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### 1. INTRODUCTION

Gas discharges at low pressures and temperatures (cold plasmas) are being used in a diverse and expanding number of applications that have in common the objective of modifying the surfaces of materials. These applications involve a variety of physical and chemical interactions of plasmas with solids and cover a broad spectrum of topics. It is not our intention to provide an inclusive or exhaustive coverage of the subject matter. Rather, we shall focus on a few applications that illustrate some of the unique capabilities of plasmas to modify surfaces and to produce end products with very substantial technological and economic significance.

Modifications of solid surfaces arising from interactions with cold plasmas can be broadly classified as surface cleaning and alteration, chemical alteration, etching, film deposition and texturing. Cold plasmas are used to remove trace contaminants and to produce rearrangement of atomic or molecular configurations, usually in preparation for further

processing of the surface. Examples include the removal of contaminants from substrates prior to film deposition (see for example ref. 1) and the treatment of polymers to increase wettability or to produce molecular weight changes in near-surface regions [2]. The chemical composition of surface and near-surface regions can also be altered by interactions with plasmas. Oxidizing (e.g. by plasma anodization), nitriding, carbiding and siliciding of metal or semiconductor surfaces are examples of such alterations [2]. Atom-by-atom etching of surface material can result from physical and/or chemical interactions with plasmas. Plasma-assisted etching methods, such as ion beam etching, plasma etching and reactive ion etching are becoming indispensable techniques for the fabrication of micro-electronic devices, particularly silicon integrated circuits [3]. Plasmas are also widely used for the deposition of thin films on surfaces (ref. 4, Parts II and IV). Deposited films serve various functions ranging from surface protection against corrosion and wear to active and passive elements in electronic,

magnetic or optical devices. Plasma polymerization, plasma-assisted chemical vapor deposition (PACVD), sputter deposition and ion plating are the more important techniques employed. Finally, surface topography can be altered by interactions with a plasma. Both etching and deposition are usually involved in texturing.

## 2. THE CHARACTERISTICS OF NON-EQUILIBRIUM PLASMAS

Plasmas of interest for surface modification are low pressure (glow) discharges. Operating pressures range from about  $10^{-4}$  Torr to 10 Torr, depending on the application. These plasmas contain free electrons, positive and negative ions, neutral atoms and, in molecular gases, neutral molecules and molecular fragments (including free radicals) produced primarily by electron impact dissociation. Average electron energies range from about 1 to 10 eV, while the energies of ions and neutrals in the bulk of the plasma are substantially less (about 0.1 eV). Thus the plasma is effectively "cold" even though the electron energies correspond to temperatures up to about  $10^5$  K.

Various kinds of reactor have been used with r.f., d.c. and microwave discharges providing the plasmas. Typical reactors are shown in Figs. 1-5. When an r.f. potential is applied to a parallel plate reactor of the type

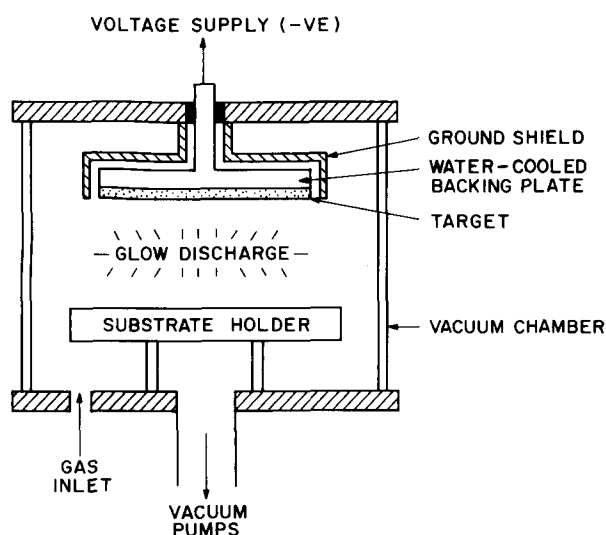


Fig. 1. Schematic diagram of a sputtering system.

shown in Fig. 3, the two electrodes alternately become the anode and the cathode on each half-cycle. If the two electrodes are of equal areas, the processes occurring at each will

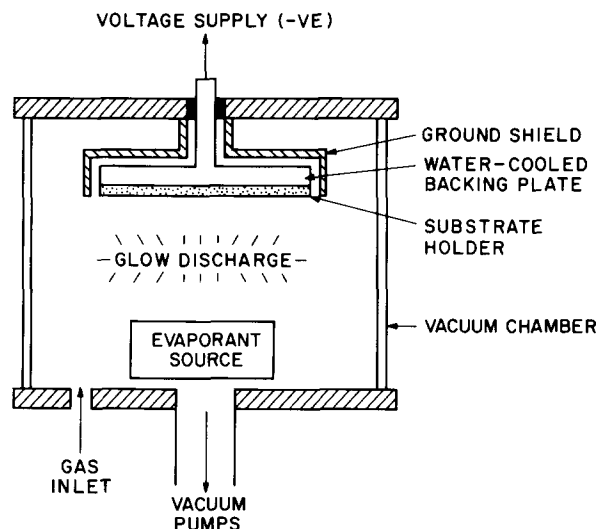


Fig. 2. Schematic diagram of a system used for ion plating.

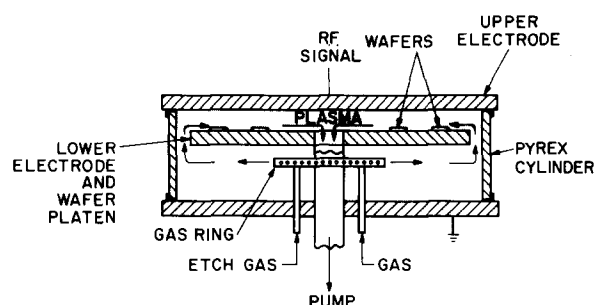


Fig. 3. Schematic diagram of a plasma reactor which uses r.f. power (radial flow).

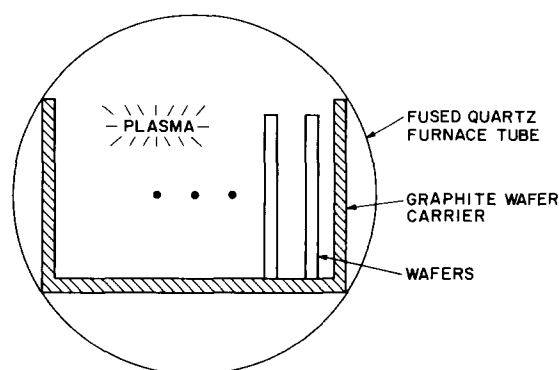


Fig. 4. Schematic diagram of a longitudinal flow plasma reactor.

tend to be identical despite the fact that one may be grounded. This occurs because the plasma potential in such a system is always more positive than that of the most positive electrode. Thus, as the driven electrode becomes an anode, the plasma potential rises so that a cathode sheath with a potential drop equal to essentially the full zero-to-peak applied potential develops at the grounded electrode, as shown in Fig. 6(a). It can also be seen in the figure that the time-averaged potentials of the electrodes are negative

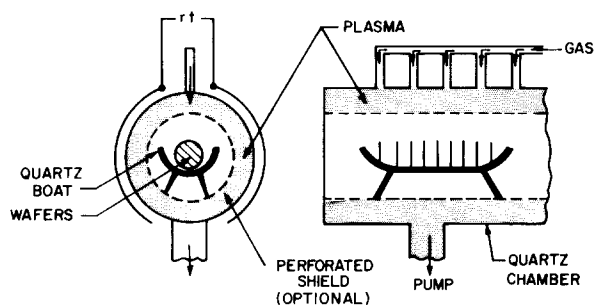


Fig. 5. Schematic diagram of a barrel reactor used for plasma etching.

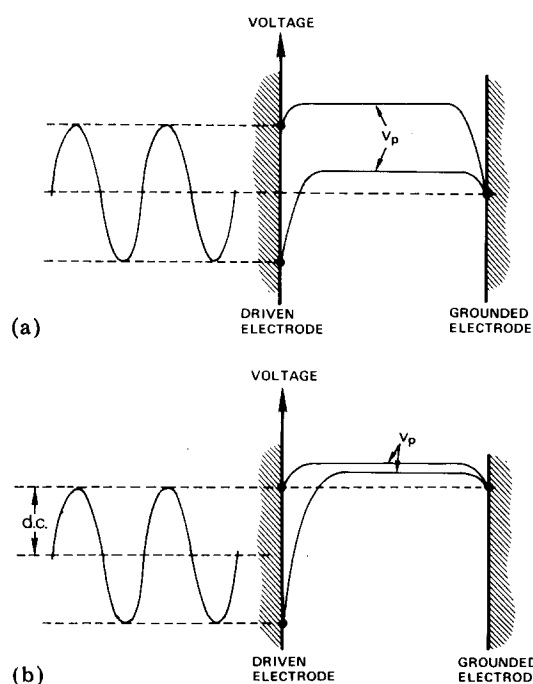


Fig. 6. Plasma potentials with respect to anode and cathode: (a) the driven electrode area equals the grounded electrode area; (b) the driven electrode area is much smaller than the grounded electrode area.

relative to the plasma potential. When the electrodes are of unequal areas, the distribution of potential between the two electrodes will depend on their relative areas in contact with the plasma, with the smaller electrode being at a larger average negative potential relative to the plasma potential, as shown in Fig. 6(b). The configurations of many reactors are such that the electrodes are of nearly equal areas and the substrates are subjected to considerable ion as well as electron bombardment. Accordingly, both plasma-volume and plasma-wall reactions are of critical importance in determining surface properties.

Free electrons are the energetic species in plasmas. They gain energy from the electric field faster than ions do and are thermally isolated from atoms and molecules, as far as elastic collisions are concerned, by the mass difference. Consequently, the electrons accumulate sufficient kinetic energy to undergo inelastic collisions and to produce the ionization required to sustain the plasma. The relevant energy flow is therefore primarily from the electric field to the electron gas, from the electron gas to the molecular gas, and finally from the molecular gas to the substrates and reactor walls in the form of ions and molecular radicals. Typical classes of plasma-volume reactions are listed in Table 1.

Although several of the important reactions, such as metastable induced excitation or ionization, ion-molecule reactions and radical associations, involve strictly heavy particle collisions; electron impact excitation, ionization and dissociation are the precursors to all these reactions. Thus, reactions involving the free electrons determine the ultimate composition of the species which arrive at the

TABLE 1

Volume reactions

Electron impact ionization	$e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2e^-$
Electron dissociative excitation	$e^- + \text{CF}_4 \rightarrow \text{CF}_4^* + e^-$ , $\text{CF}_4^* \rightarrow \text{CF}_3 + \text{F}$
Electron dissociative attachment	$e^- + \text{O}_2 \rightarrow \text{O}_2^-$ , $\text{O}_2^- \rightarrow \text{O}^- + \text{O}$
Dissociative recombination	$\text{N}_2^+ + e^- \rightarrow 2\text{N}$
Metastable induced ionization	$\text{He}^* + \text{X} \rightarrow \text{X}^+ + e^- + \text{He}$
Ion-molecule reaction	$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$
Radical association	$\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{Si}_2\text{H}_6$

substrate. The state of the electron gas, and therefore the character of its interaction with the molecular gas, is determined by the electron density and the electron energy distribution function [5]. The electron energy distribution function, rather than an electron temperature, is required to describe the electrons because of the non-equilibrium character of the plasmas. The electron energy distribution function may be determined in principle by solving the Boltzmann equation. The Boltzmann equation balances all processes which feed energy into and out of the electron gas at each point within the plasma discharge. Such an analysis, therefore, requires knowledge of the electron collision cross sections for all the relevant atomic and molecular species, the detailed reactor geometry and the temporal variation in the electric field within the geometry. The complexities are obvious

### 3. PROCESSES AND APPLICATIONS

Several processes will now be described for modifying solid surfaces with plasmas that illustrate the various physical and chemical phenomena involved and the extremes in our knowledge of the processes which range from relatively well understood to the relatively poorly understood.

#### 3.1. Sputter deposition of films (*ref. 4, Part II*)

Figure 1 illustrates a simplified cross section of a sputtering system. The target consists of the material to be deposited or from which the film will be synthesized in a reactive sputter deposition. A gas is introduced to the vacuum chamber at a pressure ranging from a few millitorrs to about 100 mTorr, and a discharge is ignited by applying a d.c. or r.f. voltage of sufficient magnitude. The power is coupled to the target so that the target is negatively biased with respect to the plasma. With proper system geometry and grounding, most of the applied voltage drops across a narrow (about 1 cm) sheath between the target and plasma. Under these conditions, positive ions are drawn from the plasma, accelerated across the sheath and impact the target surface. When the arriving ions have

energies exceeding a certain threshold value (the sputtering threshold which is typically tens of electronvolts), they can cause ejection of target atoms. The ejected atoms condense on all surfaces that they encounter. Thus a film can be grown, atom by atom, on the substrate.

In practical systems, argon is most often used as the gas, and the bombarding ions can have energies up to several kiloelectronvolts. Reactive sputtering is a useful variant where the gas used contains one or more constituents that can react with the target material to form a compound. For example,  $\text{TiO}_2$  films can be deposited by sputtering titanium in oxygen or Ar- $\text{O}_2$  mixtures, and  $\text{Si}_3\text{N}_4$  films result when silicon is sputtered in nitrogen or  $\text{NH}_3$  discharges.

In practice, magnetic fields are often used to enhance the rate of sputter deposition. An important configuration of this type is known as magnetron sputtering. The fields are usually applied by fixed permanent magnet pole pieces in close proximity to the target and impart a helical motion to the free electrons of the plasma. This has the net effect of increasing the electron path length, thereby causing an increase in the number of ionizing collisions and the plasma (ion) density. An added benefit of magnetron sputtering is a reduction in the number of high energy (secondary) electrons reaching the substrate after ejection from the target. This reduces substrate heating considerably and makes possible the deposition of films onto thermally sensitive substrates, such as polymers, without elaborate means of heat dissipation.

Sputter deposition is a relatively well-characterized and well-understood process. It offers certain advantages in comparison with other film formation techniques. For example, sputtering is applicable to any material if an appropriate target can be fabricated. Furthermore, compounds and multielement materials can be sputtered, and films can be deposited with the stoichiometry of the target. An additional advantage is that the sputtered atoms typically arrive at the substrate with much greater energy than is obtained with other deposition techniques. This often results in improved adhesion of films.

Sputtering is widely employed in the metals, plastics, optics and microelectronics industries using a variety of commercial equip-

ment. Applications include decorative and protective coatings, dielectric films for insulation and optical components, metallic films for magnetic or electronic circuit elements, and wear coatings for tools. The magnitude of the effort in this area is indicated by the fact that the sale of sputtering equipment to the semiconductor industry alone is estimated to total U.S. \$300 million per year by 1985.

### 3.2. Sputter etching

The sputtering phenomenon is also used to remove surface material under conditions quite similar to those just described for sputter deposition. In essence, the target becomes the workpiece. A noble gas discharge is usually employed, and material is removed by a strictly physical interaction between energetic ions extracted from the plasma and the solid surface. An important feature of this interaction for some applications is that ions arrive predominantly at normal incidence to the surface. Thus the etching is strongly directional (anisotropic). Anisotropic etching is particularly pertinent to certain microelectronics applications where etching is used to transfer very fine (micrometer-sized) patterns into the surface by use of an expendable patterned masking layer, typically an organic photoresist. A high degree of etch anisotropy ensures that the etched feature will not undercut the mask and diminish pattern fidelity [6].

Sputter etching also has several drawbacks in connection with pattern transfer for microelectronic devices. Most importantly, it is not very selective. Because it is a strictly physical process, the etch rates for different materials do not differ by much. As a result, sputter etching cannot be used in a typical integrated circuit fabrication step, such as etching of contact windows through an  $\text{SiO}_2$  film to expose shallow junctions in an underlying silicon substrate, without etching away an unacceptable amount of the junctions. Newer techniques that rely on both physical and chemical interactions via reactive plasmas are preferable in these applications and will be discussed later. However, sputter etching continues to be used where reactive plasmas with suitable chemistries are not known, as in some of the fabrication steps for GaAs, magnetic bubble and integrated optical devices. For example, a key step in the fabrication of a magnetic

bubble memory chip is the delineation of a pattern of microscopic elements with dimensions of the order of  $1\text{ }\mu\text{m}$  in a magnetic NiFe film with a thickness of the order of  $\frac{1}{2}\text{ }\mu\text{m}$ . Up to 4 million elements may reside on a chip area of about  $1\text{ cm}^2$ . Sputter etching is used by some manufacturers of bubble memories to produce this pattern.

Sputter etching is also useful for cleaning surfaces, particularly for the removal of trace contaminants and thin insulating layers from metal and semiconductor surfaces. In these applications, sputter etching usually takes place *in situ* and just prior to film deposition. A typical application is the deposition of a metal film over an existing metal film or semiconductor surface for the purpose of making an electrical contact. Contaminants or thin interface layers must be removed prior to deposition to obtain an acceptably low contact resistance.

### 3.3. Ion plating

Ion plating refers to a technique in which an evaporant stream is condensed on a substrate which serves as the cathode in a plasma discharge, typically in argon [7] (Fig. 2). The evaporant atoms (molecules) pass through the plasma in transit and some of them are ionized. The ionized evaporant atoms are accelerated into the substrate by the applied potential and become intermixed with near-surface regions of the substrate, forming a graded interface. This effect leads to superior adhesion and the possibility of forming novel non-equilibrium "alloys" in the intermixed region. The condensing film is simultaneously sputter etched, primarily by argon ions, and some of the sputtered material redeposits onto adjacent areas of the substrate which may be shielded from the evaporant beam. The net effect of this simultaneous deposition and etching is a high degree of coating uniformity and "throwing power". A successful commercial application is the McDonnell-Douglas process called "Invadizing" [8]. The process uses ion plating to deposit a dense adherent coating of aluminum on metal aircraft components to protect them from corrosion. Ion plating has also led to a new class of alloy coatings for gas turbine components which have the composition  $\text{M-Cr-Al-Y}$  where M can be almost any element. Similar processes for protection against wear and corrosion are

found in the electrical connector and fastener industries.

A broader definition of ion plating that some advocate includes any film deposition process in which energetic ions bombard the substrate surface during deposition. A subset of this definition is bias sputtering in which a film is sputter deposited onto a substrate that is externally biased with respect to the plasma to promote bombardment by low energy ions. This results in a continuous process of sputter deposition and sputter etching at the substrate that is useful in reducing the impurity content and increasing the density of the deposited film, as well as in obtaining better coverage of surface topography. An illustrative application of this technique is the formation of so-called "titanium gold" for coating jewelry. The deposited film is actually titanium nitride. The optical properties of this material impart a distinctive golden color to films of appropriate thickness and purity. The proper color is much easier to obtain if the deposited films are free of oxygen contamination from background gases.

Most films deposited by sputtering or evaporation are in a stressed state. This stress can limit the practical thickness of a deposited film because the shear forces ultimately overcome adhesive forces and produce delamination. It has been observed that the sign (tensile or compressive) and magnitude of stress can be altered when deposited films are simultaneously bombarded by low energy ions. This approach allows the deposition of thick coatings of chromium, for example. Similarly, the microstructure and/or stoichiometry of films can be altered by simultaneous ion bombardment during deposition.

Two phenomena of importance in ion plating, sputter etching and ionization in a glow discharge, are relatively well understood. However, the mechanisms by which simultaneous ion bombardment influences film properties and characteristics, such as stress, stoichiometry and microstructure, are not adequately known.

### 3.4. Plasma oxidation

Plasma oxidation is a low temperature vacuum process for the growth of native oxides on metals and semiconductors. It is a good example of chemical alteration of surfaces by interaction with a plasma. For

instance, silicon wafers can be oxidized at a reasonable rate with substrate temperatures below 600 °C, thus reducing wafer warpage, dopant diffusion and generation of defects such as stacking faults. Unlike thermal oxidation, it is an anisotropic process which minimizes lateral oxidation beneath the mask (the so-called "bird's beak" effect). It is also compatible with other dry processes, such as plasma etching and ion beam sputtering. Compound semiconductors require low temperature surface preparation techniques because of their low evaporation temperatures. Plasma oxidation has also been used extensively in the Josephson junction technology where oxides of precise thickness and high tolerance to temperature recycling must be formed. Theoretical models for plasma oxidation are currently being developed [9].

When a substrate such as silicon is placed in an oxygen plasma, the surface is often negatively charged with respect to the plasma as a result of higher electron mobility. Unless the silicon surface is biased with respect to the plasma potential, it is continuously bombarded by both positively and negatively charged plasma particles, as well as by neutral oxygen species. As a consequence of these interactions, the surface is oxidized to a few tens of ångströms because of low energy implant, diffusion and chemical reactions. Further growth is made by positively biasing the substrate with respect to the plasma so as to collect negatively charged species. Oxides can be grown in this way (anodization) to thicknesses exceeding 1 µm. The rate of oxide growth strongly depends on the  $O_x^-$  flux available at the silicon surface, and the rate of transfer (drift and diffusion) of these active charged species across the oxide to the Si-SiO<sub>2</sub> interface for the formation of native oxide. Thus the important parameter for the oxide growth at low temperatures is the strength of the electric field impressed across the oxide. Of course, increasing the substrate temperature will also increase the oxidation rate via diffusion. Although oxygen plasmas do possess a small fraction of negatively charged ions, it has been determined that the main source of negative oxygen species is created on the surface of the substrate as a consequence of electron capture by adsorbed oxygen atoms or molecules [10]. Thus the plasma electron density and its energy distribution are impor-

tant parameters for the optimization of the surface electron capture cross section. Unlike the case of wet chemical anodization when the substrate is biased to collect negatively charged species, the current is largely composed of electrons (more than 95%), and therefore the current efficiency is very low (only a few per cent at best). This problem can be overcome, however, by using an electron filter, such as a thin film of  $\text{ZrO}_2$  on silicon. Recently, it has been shown that by using such a filter the oxidation rate can be increased by an order of magnitude as a result of blocking the electron flow and thus increasing the electric field to about  $10^7 \text{ V cm}^{-1}$  in the oxide [11, 12]. In compound semiconductors, it has been found that both oxygen and substrate ions move in the oxide under the applied electric field [13]. This behavior greatly complicates the model for oxidation. However, it has recently been shown that, even under such complex situations, a single moving species model can accurately describe the gross features of the oxidation [14]. The basic difference between the oxidation mechanism in silicon and that in compound semiconductors is that the different elements in the compound semiconductors are oxidized at different rates.

Plasma oxidation of silicon was first carried out successfully by Ligenza [15] in 1965, using a microwave discharge. Since then, there have been numerous publications using various kinds of discharges (from d.c. to microwave) and a wide range of operating parameters [16]. For instance, the oxygen gas pressures used in these experiments varied from  $10^{-3}$  Torr to a few torrs. The substrate temperature was varied from 40 to 600 °C, while the sample was either biased or floating with respect to the oxygen plasma. The growth rates varied from linear to parabolic, indicating that the  $\text{SiO}_2$  could be formed by a combination of sputter deposition and complex growth mechanisms (such as space charge effects). Recently, Ray and Reisman [17] have reported growth of oxide on silicon wafers 57 mm in diameter in an electrodeless plasma with an oxygen pressure of more than 10 mTorr. In this case the plasma was excited by an external r.f. coil at one end of a quartz tube and the charged species diffused into the region where the tube was heated by an oven. The substrate temperature could be varied in the range

300–600 °C and the r.f. (0.5–3 MHz) power was 1–7 kW. By placing the silicon wafer close (1–2 cm) to the r.f. coil, Ray and Reisman observed oxide growth on the surface facing away from the dense plasma (which is most intense under the r.f. coil). Much thinner oxide was found on the surface facing the plasma. In this geometry, it is most likely that the plasmas on either side of the wafer have different potentials, thus creating an electric field across the silicon substrate and causing the oxide to grow. This electrodeless scheme is necessary for maintaining high oxygen purity in the oxidation chamber, and it is also attractive for scaling up the machine. A typical parabolic-like growth rate is observed with an initial rate of about  $1000 \text{ Å h}^{-1}$ . The physical properties of these oxides are very similar to those of thermal oxides, but with added benefits. For example, no dopant diffusion or oxidation-induced defects were observed. More recently, Ho and Sugano [18] have reported the growth of high quality  $\text{SiO}_2$  in a low frequency (420 kHz) r.f. discharge used for the fabrication of devices and integrated circuits. They have demonstrated that  $\text{SiO}_2$  films  $1 \mu\text{m}$  thick (for isolation purposes) can be grown in less than an hour without the bird's beak effect. Formation of high quality insulators on compound semiconductors is an important step in the fabrication of integrated circuits with these materials. Because of their low evaporation temperatures, growth of native oxides on compound semiconductors by conventional thermal oxidation has not been successful. However, during the past few years, studies of plasma grown oxides on various compound semiconductors (e.g. InP, GaAs,  $\text{In}_{1-x}\text{Ga}_x\text{As}$ ,  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  etc.) have been carried out. The properties of plasma-grown GaAs oxides have been studied in detail [19]. In particular, a combination of Rutherford backscattering and ion-induced X-ray measurements shows that the bulk of the oxide is composed of  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ . Quantitative Auger depth profiles of a typical oxide of about  $1600 \text{ Å}$  show that it is very uniform in composition and possesses a very sharp interface (of the order of  $20 \text{ Å}$ ). However, careful examination of the interface shows that there are excess amounts of arsenic over gallium in this region, i.e. the concentration ratio of arsenic to gallium is greater than unity. This non-stoichiometry is a consequence of the



thermodynamics and kinetics in the oxidation process. Although this amount of elemental arsenic is only of the order of one monolayer, it produces deleterious effects on the electrical properties of the film. On thermal annealing in inert gases (*e.g.* nitrogen, argon or helium), elemental arsenic forms metallic domains at the interface, which cause a large hysteresis (over 1 V) in the capacitance-voltage ( $C-V$ ) curve [20]. In contrast, annealing in pure hydrogen does seem to remove the elemental arsenic, but it also reduces the bulk oxide. Oxides annealed in hydrogen do not possess a large hysteresis but tend to be quite leaky because of the reduction in density (about 30%).

Chang *et al.* [21] developed a technique which illustrates the versatility of the plasma oxidation technique whereby the elemental arsenic layer could be removed or transformed into another compound during oxidation. It is well known that oxides on GaAs tend to pin the Fermi level at the semiconductor surface. Thus, adding a new layer between the oxide and the GaAs surface might overcome this problem. The key to the success of such an endeavor was the identification of the proper reactant. The desirable properties of the reactant are as follows. First, it should be a gas which can form a plasma that can coexist with the oxygen plasma without reacting with it. Secondly, the reactant should react more readily with arsenic than with gallium. Lastly, this added reaction should not compete with the formation of arsenic oxide. An element that satisfies these conditions is fluorine. Therefore, oxides were grown using a fluorinated oxygen (*e.g.*  $CF_4$  in oxygen) discharge. Chemical depth profiles through an as-grown oxide, obtained using Auger analysis, show that the amount of fluorine is almost 6 at.% and that the oxide is essentially stoichiometric (except for the presence of fluorine), *i.e.* the gallium-to-arsenic concentration ratio is nearly unity all the way through the interface region. An oxyfluoride film has been formed at the interface [22]. Ellipsometric measurements show that oxides with fluorine are more transparent and that the absorption edge is shifted toward higher energies, indicating the removal of elemental arsenic [23]. A typical high frequency (1 MHz)  $C-V$  curve shows essentially no hysteresis (in contrast with the case without fluorine), indicating that the selective

oxidation process has removed most of the trap states. The  $C-V$  curve goes into "inversion" at negative bias, indicating that the oxide does not leak [24]. Thus, it has been shown that the GaAs-oxide interface properties can be modified by a selective plasma processing technique. More recent results have also confirmed these observations [25]. Following the favorable results of plasma oxides grown on GaAs, oxygen plasmas have also been successfully used to grow native oxides on InP,  $In_{1-x}Ga_xAs$  and  $Cd_xHg_{1-x}Te$ . Using the native oxides as a gate dielectric, field effect transistors have also been fabricated on these materials [26].

### 3.5. Surface preparation and passivation

Surface preparation and passivation of semiconducting (especially compound semiconductors) materials using plasmas is a relatively new area of research. Unlike silicon, compound semiconductors have a very low evaporation temperature (500 °C or less) and it is difficult to remove surface contamination (such as carbon) and native oxides. However, recent experiments have demonstrated that, by using hydrogen plasmas, surface carbon and native oxides can easily be removed from compound semiconductor surfaces near room temperature [27]. These results are significant in that, by removing the native oxide first, it is then possible to form a nitride surface using nitrogen plasmas when needed. This is a very crucial step in passivating compound semiconductor surfaces for integrated circuit technology. Preliminary results show that this procedure is very useful in improving the device characteristics. The detailed mechanisms in these plasma surface preparation studies are not well understood at this point.

### 3.6. Plasma-assisted chemical vapor deposition

PACVD is a process in which a glow discharge plasma is used as a catalyst to promote the formation of a coating from constituents carried in the gas phase to the substrate [28–31]. PACVD differs from conventional chemical vapor deposition in that coatings can be deposited at much lower substrate temperatures. For example, a substrate temperature of about 700 °C is required to deposit silicon at a rate of about 1 nm s<sup>-1</sup> via the pyrolyzation of silane ( $SiH_4$ ). However, if the  $SiH_4$  is passed through a low pressure plasma discharge in

the vicinity of the substrate, radicals created in the discharge can be condensed at room temperature to form silicon coatings at a similar deposition rate. The plasma volume and substrate surface reactions in PACVD are driven by kinetic processes, rather than the more nearly equilibrium thermodynamic processes that characterize conventional chemical vapor depositions. Accordingly, an almost unlimited number of gases appear to be candidates for introducing coating materials into PACVD deposition reactors. Typical coatings and the associated working gases are given in Table 2.

The low temperatures that are used in PACVD yield materials that, in general, are very different from their bulk counterparts and that probably should be considered as a generic class of materials in themselves. Most notable are the observations that, first, PACVD coatings often contain large amounts of entrapped working gas species that were not released at the low deposition temperatures and, secondly, PACVD coatings of compounds are generally amorphous. This is in contrast with conventional chemical vapor deposition, where the high deposition temperatures tend to yield coatings with bulk material properties.

Despite these rather unique properties, PACVD coatings have found use in several important industrial applications. In fact, it is these very properties, together with the low deposition temperatures, that have led to many of the applications with the promise of more in the future. Thus, PACVD silicon nitride films have been found to provide excel-

lent barriers to moisture and alkali ions and are becoming widely used as microcircuit passivation layers. An important aspect is the fact that the PACVD coatings can be deposited at sufficiently low temperatures to avoid distributing the aluminum metallization that is present on the wafers at the time of passivation. Similarly, PACVD silicon oxide films are being used as interlayer dielectrics and as masking layers during microcircuit fabrication. Of particular importance in these applications is the observation that PACVD coatings appear to be conformal and less vulnerable to pinholes than coatings deposited by evaporation or sputtering [31]. PACVD amorphous-carbon-coated IR optical systems are now commercially produced.

The deposition of hydrogenated amorphous silicon (a-Si:H) constitutes a potentially very important PACVD application. Under certain conditions of deposition, some of the residual hydrogen that is entrapped with PACVD silicon is bonded at the "vacancy" sites that tend to be created by the amorphous structure. Accordingly, these dangling bond sites, which would otherwise produce energy levels within the band gap and therefore compromise the semiconducting properties of the amorphous silicon, are effectively "passivated" by the hydrogen. The density of such mid-gap states can be reduced to the  $10^{15} \text{ cm}^{-3}$  range, with the consequence that a-Si:H can be doped n or p type, and electronic devices such as solar cells can be fabricated [32]. Thin film a-Si:H solar cells are widely used today in small calculators [33]. Efficiencies in the 10% range have been achieved in the laboratory [34], and this technology shows great promise for the fabrication of low cost solar cells for large-scale power generation. PACVD polycrystalline silicon thin film transistors have also been fabricated [35].

Future PACVD applications could involve the deposition of metal silicide interconnects and metallic gate materials for very-large-scale integrated circuits as well as epitaxial growth of semiconducting crystalline films. Another class of applications could involve the deposition of wear-resistant coatings for substrates such as tool steels where the use of conventional chemical vapor deposition temperatures would destroy the properties achieved in previous heat treatments. With respect to the last point, it is interesting to note that PACVD

TABLE 2

Typical materials deposited by plasma-assisted chemical vapor deposition

<i>Coating material</i>	<i>Working gases</i>
$\text{Si}_3\text{N}_4$	$\text{SiH}_4 + \text{N}_2$ , $\text{SiH}_4 + \text{NH}_3$
$\text{SiO}_2$	$\text{SiH}_4 + \text{O}_2$ , $\text{SiH}_4 + \text{N}_2\text{O}$
SiC	$\text{SiH}_4 + \text{CH}_4$ , $\text{SiH}_4 + \text{C}_2\text{H}_2$
a-Si	$\text{SiH}_4 + \text{Ar}$
a-C	$\text{C}_4\text{H}_{10}$
a-As	$\text{AsH}_3 + \text{Ar}$
$\text{Al}_2\text{O}_3$	$(\text{AlCl}_3)_2 + \text{O}_2$
BN	$\text{BCl}_3 + \text{NH}_3 + \text{H}_2$
$\text{SnO}_2$	$\text{Sn}(\text{CH}_3)_4 + \text{O}_2$

a-Si, amorphous silicon; a-C, amorphous carbon; a-As, amorphous arsenic.

TiC coatings with relatively high hardnesses have been reported [31, 36], despite the amorphous structures and sub-bulk densities that tend to characterize PACVD materials. So-called "diamond-like" amorphous carbon coatings are attracting considerable attention [31].

The potential uses of PACVD films for microelectronics applications warrants some additional discussion. As noted previously, PACVD dielectric films have become used extensively in fabricating silicon integrated circuits. They are also used in fabricating discrete optoelectronic devices. The low deposition temperature, discussed above, is a key aspect in these applications. With the exception of the amorphous silicon thin film solar cells, PACVD films have not been used where the film electrical characteristics are critical to device performance, at least for the silicon integrated circuit applications pursued thus far. The submicrometer integrated circuits of the future will place increasingly severe demands on the electrical properties of the various films used in their fabrication. The PACVD process will need to be improved to meet these challenges. One of the major disadvantages of PACVD for integrated circuit device fabrication is that the plasma induces charged defects onto the substrate surface, as well as in the dielectric film itself during deposition. An answer may lie in using the capabilities of PACVD to generate active chemical species which are reacted at a substrate surface that is not in contact with a plasma. A recent experiment illustrates the possibilities of using well-characterized atomic beams. Atomic beams of several metals were reacted with atomic beams of nitrogen and oxygen to form thin films of oxides and nitrides [37]. Characterization of the resultant films, which were formed at low substrate temperatures, indicated that they were of high quality with close to bulk physical properties.

### 3.7. Plasma-assisted etching [3, 6]

In plasma-assisted etching a molecular gas plasma serves as a source of reactive radicals capable of chemically combining with a solid surface to form a volatile product readily removed by pumping. Silicon, for example, can be etched in a  $\text{CF}_4$  discharge with gaseous  $\text{SiF}_4$  as a byproduct. The essential chemical reaction is with the fluorine atoms generated

in the plasma by the electron impact dissociation of  $\text{CF}_4$  molecules. The development of plasma-assisted etching has been motivated primarily by the needs of silicon integrated circuit technology.

Various methods for implementing plasma-assisted etching have been devised, leading to a variety of equipment and terminology; plasma etching and reactive ion etching (reactive sputter etching) are the most frequently used terms. The earliest equipment was the barrel reactor (Fig. 5), a fused quartz cylinder within which an electrodeless r.f. discharge is maintained. The material to be etched is immersed in the plasma and allowed to float electrically so that the ions bombarding the surface are of low energy. Etching in barrel systems is isotropic, *i.e.* the etch rate of a material is independent of direction. Consequently, barrel reactors are not used for critical pattern transfer operations requiring high resolution but are widely employed for low resolution etching and plasma stripping of photoresist masks. In 1982, U.S. manufacturers of barrel reactors sold approximately 500 systems at an average price of U.S. \$30 000, giving a gross income of approximately U.S. \$15 million.

As the technology evolved, emphasis shifted to parallel electrode systems. In these the plasma is usually generated by coupling r.f. power into a gas confined between two parallel electrodes (as in Fig. 3) or between a single electrode and a grounded vacuum chamber (similar to Fig. 1). The material to be etched is placed on either the powered or the grounded electrode (both electrodes are bombarded with ions for a system of nearly equal electrode areas as discussed in Section 2). The former arrangement is termed reactive ion etching and the latter plasma etching. It soon became apparent that the etching in such systems could be highly directional (anisotropic). Directionality was correlated with the bombardment of the etching surface by energetic ions [38] which, as in sputter etching, impinge on the surface predominantly at normal incidence. The ions are not the primary etchant species but rather serve to enhance or even to induce reactions between the solid and reactive species generated in the plasma.

Ion-assisted chemical reactions have two important attributes which have had a dramat-

ic impact on integrated circuit technology. First, etch rate anisotropy is attainable. In particular, it is possible to etch through the thickness of a material with essentially no lateral etching. As noted earlier in the discussion of sputter etching, highly anisotropic etching becomes essential for pattern transfer operations as the size of circuit features is scaled down to achieve higher circuit densities and greater performance-to-cost ratios. Second, but of no less importance, etch rate selectivity between different materials can be obtained because etching occurs through a chemical reaction. This makes possible the patterning of high aspect (depth-to-width) ratio features in a material which overlays a thin layer of dissimilar material without significant removal of the underlying layer. This task must be accomplished several times with critical dimensional control in the fabrication of an integrated circuit. For example, in a state-of-the-art memory device such as a 256k dynamic random access memory, more than a quarter of a million pieces of information can be stored on a "chip" smaller than a thumbnail. Such a chip may contain some 600 000 circuit elements with minimum dimensions of 1.5–2.0  $\mu\text{m}$  that must be controlled to  $\pm 0.3 \mu\text{m}$  or better.

The need for high resolution (anisotropic) etching in integrated circuit fabrication and the unique ability of plasma-assisted etching to provide it has spawned a highly competitive market-place for plasma etching equipment over the past 5 years. At present, there are more than 60 companies world-wide which either manufacture equipment for plasma-assisted etching or are actively contemplating entry into the market. Because the development of the technology has been largely empirical, available equipment is quite diverse with no clearly established preferences, as yet. Thus, it is entirely likely that there will be additional entries into a market estimated to reach U.S. \$ $\frac{1}{4}$  billion by 1986. Ultimately, the equipment market probably will be dominated by a few manufacturers.

The explosive growth, pervasive influence and strategic importance of integrated circuits are well known. At the present rate of growth, the sales of integrated circuits will reach U.S. \$50 billion annually by 1990. It is fair to say that today's leading integrated circuits products (domestic, Japanese and European)

would not exist without plasma-assisted etching and that continued progress in integrated circuits will be tightly coupled to further development of plasma technology. Further development would be greatly expedited if a better base of understanding was available. As with plasma deposition, a large number of often interdependent variables influence plasma-assisted etching. Despite substantial advances in basic understanding over the past several years, the process complexity still necessitates a largely empirical approach to the development of plasma-assisted etching techniques.

Plasma-assisted etching is also being used or explored for other solid state device technologies, such as bubble memories, III–V and II–VI compounds, integrated optics and displays. However, the applications have been more limited and of substantially less economic importance. This is due in part to the limited effort expended. Each of these technologies presents unique problems that must be considered. Experience in silicon technology is helpful in providing guidance but, unless a better base of understanding becomes available, a realization of the true potential for applications of plasma-assisted etching to these and other solid state technologies will be won only through hard-fought empirical battles. This implies expenditures of time and effort. Nonetheless, there is ample evidence of considerable promise for plasma-assisted etching in the various technologies listed here. For example, a key problem in the integration of optical sources into a chip technology is that of providing the necessary feedback for the laser structure to reach stimulated emission. One approach that has been pursued is to fabricate a Fabry–Pérot resonating cavity by reactive ion etching in mirror faces [39–41]

Another etching application involves the manufacture of multilayer printed-circuit boards which requires the drilling of many small holes. The drilling procedure leaves deposits of organic material which inhibit subsequent plating processes. Removal of these organic deposits from drill holes by exposure to a reactive gas plasma is called "plasma desmearing" and could become a very important manufacturing procedure [42]. Similar plasma techniques are used to remove a wide variety of organic materials from surfaces and the procedure is often called "plasma ashing".

### 3.8. Plasma polymerization: significance in materials science

Plasma polymerization is a unique ultrathin film technology which yields polymers with properties completely different from those of conventional polymers [43]. Plasma polymers have no discernible repeat units and, in many cases, are formed in highly cross-linked and branched networks consisting of very short segments, even if a well-defined monomer is used as the starting material. In contrast with conventional polymers, chemical and physical properties of a plasma polymer are not solely determined by the chemical nature of the monomer. Consequently, it is not appropriate to discuss the properties of plasma polymers in general terms, such as the "plasma polymer of styrene or ethylene" etc. It is important to recognize the following major factors to evaluate and recognize the merits of plasma polymers. First, the plasma polymer of styrene is not polystyrene and, secondly, plasma polymerization of styrene does not produce a polymer which can be discerned as "plasma polymer of styrene", although such a term is commonly used to describe the products of plasma polymerization. The product of plasma polymerization varies depending on the conditions. A variety of products covering gases, oily substances, soluble polymers, insoluble coherent films, polymeric powders etc. can be formed from a monomer, *e.g.* ethylene [44]. Obviously, for membranes and protective coatings, our interests are on the coherent films formed by plasma polymerization. It should also be re-emphasized that plasma polymerization is an ultrathin film technology. Therefore the unique advantage of plasma polymerization is realized in ultrathin film applications (*e.g.* for thicknesses of 100–5000 Å, and particularly the 100–500 Å region), where the application of polymer films by conventional methods is very difficult and is often economically unfavorable. Conversely, the use of plasma polymers for application in which a thicker layer (*e.g.* of thickness larger than 1 μm) of polymer is required is not considered to be an advantageous application of plasma polymerization. Ultrathin films, thus defined, have a great potential in many practical applications. For instance, practical membrane separation processes require ultrathin films in order to have a reasonable throughput. Therefore, there is

a great potential for plasma polymers in the area of membranes for separation processes. Another important area of application where plasma polymers play a very unique role is for protective coatings and modification of surfaces. Some important aspects of plasma polymers used as protective coatings (surface modification) and ultrathin (composite) membranes will be discussed in this paper.

The protection obtainable by a barrier layer is dependent on the permeability of the polymer and the thickness of the film. Because of very small thicknesses in ultrathin coatings, the barrier protection obtainable is generally limited. The overall barrier protection obtained by a film 1 μm thick, where the permeability is one-hundredth of that for polyethylene, is identical with polyethylene film 100 μm thick. Therefore, unless an extremely low permeability can be obtained, ultrathin films generally have a limited barrier protection capability and, in many cases, conventional polymers applied in an ultrathin layer provide almost no protection against relatively small molecules such as SO<sub>2</sub>, NO<sub>2</sub>, H<sub>2</sub>O etc. Therefore the use of plasma polymers as protective coatings may be viewed in three categories: (1) limited thickness applications where thicker layers cannot be used, as is the case in the protection of magnetic discs; (2) the use of an ultrathin layer to improve overall protection of a conventional polymer layer by preventing failure of coatings; (3) the modification of surface properties to delay action of corrosive agents in liquids. In an ultrathin film the contribution of interface properties may become as important as the bulk properties of the polymer. Therefore, many important factors which contribute to the overall protection characteristics of the coatings, but have been neglected in thicker coatings, become obvious. The problems associated with protective coatings, such as adhesion to metallic substrates, barrier characteristics and surface characteristics of a coating, are greatly amplified in an ultrathin coating. Thus the studies of plasma polymers used as an ultrathin protective coating provide a unique opportunity to recognize the nature of these inherent problems from a new viewpoint.

The adhesion of protective coatings to the metallic substrate plays an essential role in the usefulness of the coatings. It is obvious that, irrespective of how good a barrier material is,

the film provides no protection if it does not adhere well to the substrate. The interface between polymer and substrate is the crucial factor in the overall coating. Although there is a trend that adhesion of a coating is judged by the adhesive strength measurement performed in air, such a dry adhesive strength could be misleading. The influence of liquid water or water vapor at the interface is more important in an actual situation than the test values in air might indicate. This is particularly true in view of the fact that a protective coating is needed in more severe environments than the air in a laboratory and that the most corrosive environments contain water in liquid and/or vapor phases.

Recent studies have indicated that there is no direct correlation between dry adhesive strength and wet adhesive strength as measured after the coatings are immersed or boiled in water [45, 46]. The most direct correlation was found between the resistance of a coating to peeling after boiling in water and the surface energy of the substrate. This correlation may be seen in the results obtained on the adhesion of Parylene polymer (vapor phase deposition of paraxylene polymer) deposited onto substrates having various surface energies, as shown in Tables 3 and 4. The details of testing methods may be seen in ref. 46. The influence of water on the polymer-substrate interface is an extremely important factor in an ultrathin film coating, since the

time lag for diffusion of water through a polymer film 0.1  $\mu\text{m}$  thick is less than a fraction of a second. Consequently, water molecules reach the interface rather quickly, and most ultrathin films have no mechanical strength to maintain the integrity of the coatings once they are peeled from the substrate. The peeling of a coating from a substrate is caused by the action of water which breaks the relatively weak interaction between polymer and substrate and forms stronger interactions between polymer and water and between water and substrate. With a thicker coating, delamination might not appear to be serious by itself since the thicker coating can maintain its integrity even if the coating is essentially delaminated. However, the effectiveness of coatings is seriously damaged by delamination because of the action of water. Water-insensitive adhesion is an important factor for effective protective coatings. Plasma polymerization provides a unique method for improving wet adhesion strength of conventional coatings by a combination of the following significant effects.

(1) Water-insensitive adhesion can be created between certain types of plasma polymer and (metal) substrate as a result of atomic interfacial mixing [48]. By this mechanism, certain types of plasma polymer can be made to adhere to a metal surface in such a manner that water does not destroy the adhesion within a practical time scale under conditions encountered in most applications.

TABLE 3

Adhesion of parylene  $\text{C}(\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2)_n$  to various substrates

Substrate	Contact angle of water (deg)	Adhesion test results <sup>a</sup>	
		Test A	Test B-1
<i>Porous</i>			
Goretex	140	5A	5B
Millipore	114	5A	5B
<i>Non-porous, smooth</i>			
Teflon	108	0A	5B
Polypropylene	100	4A	5B
Plasma polymer of methane	76	5A	4B
Poly(methyl methacrylate)	73	0A	2B
Mylar	69	0A	2B
Nylon-6	49	0A	2B
Glass	16	0A	1B

<sup>a</sup>The test results shown are expressed by a system of numerical grades which are defined in Table 4.

TABLE 4

Definitions of numerical grades used to express the adhesion test results

Numerical grade	Definition
<i>Test A (application of ANSI-ASTM Standard D 3354-76 [47] in air)</i>	
5A	No peeling
4A	Trace peeling or removal along incisions
3A	Jagged removal along incisions
2A	Jagged removal along most incisions
1A	Removal from most of the area of x-cut
0A	Removal beyond the area of x-cut
<i>Test B (boiling test in 0.9% saline solution)</i>	
5B	No lifting of the film after 3 cycles of 8 h of boiling and 16 h of room temperature soaking
4B	Lifting of the film after 3 cycles of 8 h of boiling and 16 h of room temperature soaking
3B	Lifting of the film after 1 cycle of 8 h of boiling and 16 h of room temperature soaking
2B	Lifting of the film after 60 min of boiling
1B	Lifting of the film after 15 min of boiling
0B	Lifting of the entire film almost immediately

(2) By application of such an ultrathin film, very high surface energies of metal surfaces can be converted to those of plasma polymers which have better affinity to other conventional polymer coatings. Thus, plasma polymers act as excellent primer coatings.

The effect of water-insensitive adhesion on the overall protection may be visualized by the example of a Parylene coating applied onto a platinum wire subjected to cyclic voltammetry. In the cyclic voltammetry a platinum wire coated with Parylene N (except the tip of wire) is placed in an electrolyte solution, a d.c. voltage is applied against a reference electrode and the current is read while the cyclic voltage (from  $-3.0$  to  $+3.0$  V) is applied. This process exerts an extremely severe stress on the electrode-insulator interface under the repeated anodic and cathodic reaction conditions. In Fig. 7, the current read at the  $+3.0$  V peak voltage is plotted against the number of cycles [49]. If the insulator peels off the platinum wire, the corresponding increase in the current is observed as a consequence of increased effective exposed area of the electrode. Figure 7 shows that a Parylene-N-coated platinum wire loses its insulation effect almost entirely after approximately 20 cycles, although Parylene N is one of the best polymeric insulators known today. In contrast with this situation, a composite electrode which has an ultrathin layer of plasma polymer of methane as a primer before the same

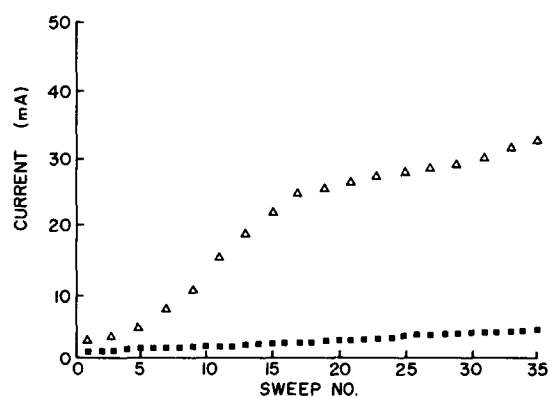


Fig. 7. Maximum current at 3.0 V d.c. vs. number of sweeps in a cyclic voltammetry experiment in 1 N  $K_2SO_4$  solution at  $25^\circ C$ :  $\Delta$ , Parylene ( $2.6 \mu m$ );  $\blacksquare$ , glow discharge polymer of methane (used as primer) ( $1000 \text{ \AA}$ ) + Parylene ( $2.5 \mu m$ ). The increase in current represents the increased exposed surface of platinum due to delamination of the coating (insulator).

Parylene N is applied shows a remarkable improvement. The composite electrode having the same insulator withstands the repeated cyclic stress in the presence of water, electrolytes and electric voltage, and the insulating function of the Parylene N coating shows little sign of failure.

These results indicate the importance of polymer-substrate characteristics and that the overall effectiveness of a protective coating is not solely determined by the barrier charac-

teristics of the coating material. As the thickness of the barrier layer decreases to the level of an ultrathin layer, the interface characteristics become more and more important since the contribution of the barrier diminishes. In other words, if some protection (*e.g.* resistance against corrosion) is to be expected from an ultrathin layer of 100–500 Å, the major protection must come from the modification of the interface to resist corrosion. It is interesting to note that ultrathin layers of plasma polymer film (thickness less than 0.1  $\mu\text{m}$ ) have given appreciable protection against the corrosion of magnetic discs (of nickel and iron) by the  $\text{NO}_2$  and  $\text{SO}_2$  in air while all other conventional polymers applied at this level of thickness have shown no effect [50]. The characteristic protection represented by the induction time of corrosion is shown in Fig. 8. This is an example which clearly shows that ultrathin films of plasma polymer are unique in providing significant protection at such a small level of film thickness. It should be reiterated that the protection obtained from such an ultrathin film is not governed solely by the low permeability of material but by more complicated combined effects of permeability, adhesion, chemical passivation of the substrate surface etc.

Plasma polymers exhibit unique bulk properties. Unlike most conventional polymers which are formed by molecular polymerization of the corresponding monomer(s), plasma

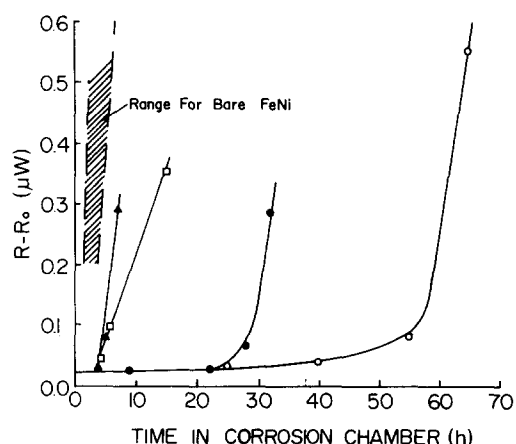


Fig. 8. The corrosion of FeNi observed by light reflectance as a function of exposure time to a glow discharge of the following gases:  $\circ$ , methane (1050 Å);  $\bullet$ , acetylene (950 Å);  $\square$ , tetramethyldisiloxane (1000 Å);  $\blacktriangle$ , tetrafluoroethylene (330 Å). The details of test method may be seen in ref. 51.

polymers have very short segments (no polymeric segments) between cross-links and are characteristically in between organic polymers (with a high long-range molecular mobility) and the inorganic materials (with no long-range mobility). The importance of such polymeric segmental mobilities and/or their absence may be visualized by examining the water vapor permeability of various polymers. The permeability of gases and vapors in a flawless polymer matrix is well established by the solution-diffusion principle [51] in which the permeability  $P$  is given by the product of the solubility  $s$  and the diffusivity  $D$ , *i.e.*

$$P = sD$$

In conventional polymers the chemical nature influences both the intermolecular interaction with other polymer molecules and also the intermolecular interaction between polymer and water. The former largely determines the diffusivity and the latter influences the solubility. For example, the polarity of polymers will increase the interaction between polymers and decrease the diffusivity, while the water-polymer interaction increases with increasing polarity of the polymer, leading to the increase in solubility. These situations may be seen in a schematic representation of  $s$ ,  $D$  and  $P$  as functions of cohesive energy density, as shown in Fig. 9. In gas permeability the gas-polymer interaction is relatively small, and its dependence on the polarity of polymers may be negligible. In such cases,  $P$  is largely determined by the magnitude of  $D$ , and consequently the use of molecular architecture to reduce the value of  $D$  would produce a good barrier material for gases. However, for water vapor which has a high polarity and has a stronger interaction with polymers (by orders of magnitude) than permanent gases do, the increase in solubility cannot be neglected. Consequently, as shown in Fig. 9,  $P$  for water vapor passes through a minimum which indicates the low limit of water vapor permeability obtainable by conventional polymers. This relationship shown schematically in Fig. 9 is indeed seen in actual polymers. In Table 5 the permeability values [51] of oxygen and water vapor are compared. The polymers are arranged in the order of increasing cohesive energy density (starting from the lowest at the top). The value of oxygen permeability decreases monotonically with the increasing



cohesive energy density, while the water vapor permeability reaches the minimum value and then a further increase in cohesive energy density actually increases the water permeability. Thus, the  $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$  ratio reaches a value of  $10^6$  for highly polar polymers such as polyacrylonitrile.

The implication of this relationship is that there is a limiting value of  $P$  for water vapor

and that it is extremely difficult to make a polymer which has a significantly lower water vapor permeability by modifying the molecular architecture as long as conventional polymers are employed. The significance of plasma polymers, in this respect, is that a different principle governs the magnitudes of  $D$  and  $s$  and, consequently, the limiting case observed with conventional polymers does not apply to plasma polymers. A value of water vapor permeability for a plasma polymer is also included in Table 5. Because of significantly lower levels of solubility, the permeation through a plasma polymer is often not truly controlled by the solution-diffusion principle. Many plasma polymers show characteristics that are between solution-diffusion-type polymers and molecular sieves. This difference in permeation mechanism might be favorably utilized in certain separation processes.

Many of the unusual or unexpected surface characteristics of polymers can only be understood by recognizing the highly perturbable or highly mobile nature of polymer molecules at the surface. In other words, the surface of a polymer solid can change its arrangement of molecules according to the change of conditions in the surrounding medium. Although the overall characteristics of a polymer molecule may be dominated by functional groups which are contained in the molecule, the surface characteristics of a solid which consists of such molecules are not necessarily determined by the overall characteristics of the molecule. If such dominating functional groups are not aligned at the surface, the surface properties

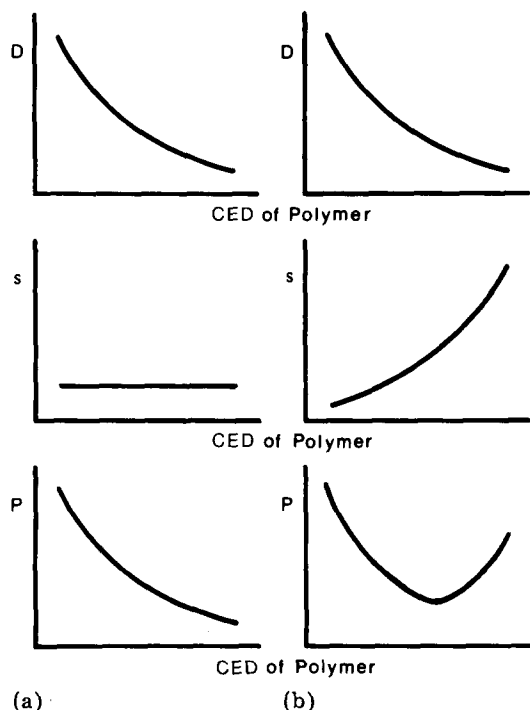


Fig. 9. Schematic representation of the dependence of  $s$ ,  $D$  and  $P = sD$  on the cohesive energy density (CED) of polymers for (a) oxygen and (b) water vapor.

TABLE 5

Oxygen permeability and water vapor permeability of polymers

Polymer	$P_{\text{O}_2} \times 10^{10}$ ( $\text{cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$ )	$P_{\text{H}_2\text{O}} \times 10^{10}$ ( $\text{cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$ )
Polydimethylsiloxane	605.0000	43000.0000
Natural rubber	23.30000	2290.0000
Polyethylene (relative density, 0.914)	2.8800	90.0000
Polytrifluorochloroethylene	0.0250	0.2900
Poly(vinylidene chloride)	0.0053	0.5000
Polyacrylonitrile	0.0002	300.0000
Plasma polymer of $\text{CH}_4$		0.0076
Sputter Cu layer		0.0026

Data at near 25 °C.

of the solid would not be determined by the functional groups. A typical example may be seen in the contact angle of water on the surface of hydrogel which contains 98% water (*e.g.* hydrogel of glycerol methacrylate). In spite of high hydrophilicity of the polymer molecule, which enables such a high-water-containing gel to be formed, a very high contact angle (greater than  $90^\circ$ ) of water is observed, indicating the extremely hydrophobic nature of the surface. This is due to the highly mobile nature (particularly of the rotational mobility) of polymer molecules, *i.e.* all hydrophilic functional groups of surface molecules are turned around as soon as hydrogel is lifted up from water to face the bulk phase of the gel where abundant water is contained [52]. A similar phenomenon, *i.e.* the burying of functional groups at the surface, can explain the decay of wettability of polymer surfaces which are given surface treatments, such as corona discharge, glow discharge and flame treatments. In other words, modifications applied to surfaces of polymeric solids are often not permanent because of the high mobility of polymer molecules at the surface. This problem can be solved by utilizing plasma polymerization as the means of producing unperturbable surfaces [53].

Properties of plasma polymers are very different from those of most organic polymers because of entirely different mechanisms of formation from those for conventional polymers. From the viewpoint of the mobility of polymer segments or atoms, plasma polymers are between organic polymers and inorganic materials. The use of such a material as a means of modifying surfaces provides a unique opportunity of solving many problems associated with the interface. Two decades ago, plasma polymerization drew the attention of scientists as an exotic means of forming polymers. However, in recent years, plasma polymerization has emerged as a unique method for forming exotic materials which have very valuable characteristics in the modification of surfaces.

### 3.9. Plasma polymerization and copolymerization: retention of structure in deposited films

The technique of plasma polymerization as a means of preparing specialty coatings of pre-

dictable structure (molecular) and properties has thus far been grossly overlooked. This neglect has stemmed, in large part, from the complexities of the plasma environment which, by virtue of its non-equilibrium nature, makes modeling of the physical and chemical processes within the discharge volume and at the walls which contain it very difficult. The presence of the sheath across which ions may be accelerated toward growing films further complicates the description of the phenomena which are contributors to the thin film deposition process.

In many applications of thin film chemistry, the chemical functionalities incorporated into the material are essential in defining its properties and dictating possible future uses of the material. In other situations the attainment of a certain chemical structure of the deposited polymer is critical, but without concern for functional group preservation during the plasma polymerization process. Thus, there are two ends of a spectrum defined by the "sought-for" characteristics of the plasma-deposited material, which in both instances require the vapor phase transport of organic or organometallic precursors into the discharge volume where they are activated by inelastic electron impact events. In one extreme, there is the wish to preserve, in large part, the molecular structure which this monomer possesses during the deposition process. As such, the characteristic chemistry associated with the functionalities already present in the monomer is carried over to and incorporated within the plasma-deposited film. In these cases, optimal energy transfer from the plasma is at a level just above the threshold for initiating and sustaining film growth. Excess energy transfer is undesirable, as it is likely to result in fragmentation of the activated monomer in ways which will cause loss of the requisite chemical functional group. In the other extreme, as discussed in the previous section, it is desirable for more extreme chemistry to occur during the deposition processes. These processes involve the activation or rupture of a larger number of chemical bonds in the monomer and, as such, the energy transfer from the discharge to the species involved in film growth must be much larger. In these cases the retention of a monomer structure is inconsequential, or even undesirable. It is the unique materials properties

which accrue to the deposited "polymer" which are of importance.

It is the former area to which the following comments are addressed. It is suggested that, at least for monomers which contain vinyl groups through which polymerization may proceed, the structural integrity of the monomer may be preserved during and after the plasma polymerization process [54-59] so as to yield a thin film having predictable chemical properties while also obtaining a high degree of cross-linking otherwise unobtainable in a straightforward number (*e.g.* by conventional condensed phase polymerization). Furthermore, there is evidence to suggest that copolymerizations of vinyl monomers are also possible in which the chemical functionalities of each of the monomers may be incorporated into these plasma-polymerized thin films [60]. Recent evidence indicating the validity of these ideas comes from research involving plasma-polymerized vinylferrocene [54-57], plasma-polymerized polystyrene [58] and plasma-polymerized vinyl dimethylethoxysilane [59] and the plasma copolymerization of vinyl dimethylethoxysilane and styrene [60]. More research in which the generality of these ideas is tested is needed.

#### 4. STATUS OF THE SCIENCE BASE: RESEARCH NEEDED

The importance of low pressure plasma processing of materials is apparent even from this brief discussion of a few representative applications. The continued development of these low pressure plasma processes will have great impact on the competitiveness and progress of high technology industries (*e.g.* the semiconductor industry) in the U.S.A. The considerable amount of money and effort expended in developing plasma technology justifies a commensurate effort in understanding the basic physics and chemistry underlying the technology.

A reasonable level of understanding is in hand for some of the technologically important processes, but for others (particularly those based on chemically reactive plasmas with applications of growing strategic importance) there remains a dearth of understanding. Plasma-assisted etching is a prime illustration of this assertion. While there have been

impressive advances in elucidating the basic phenomena governing this technology in the past few years, significant technological progress has resulted mainly from uncompromising empiricism (compare for example the state of understanding today with the perceived state of scientific needs of several years ago as stated in ref. 61). In effect, the science has not yet caught up with the technology nor indicated the way. This is not an unusual situation; indeed it is characteristic of much of modern technology development which tends to be evolutionary, but the fact is that many of the problems and obstructions to successful application of non-equilibrium plasma technology could be ameliorated by expanding our fundamental knowledge. It appears that the basic research effort world-wide is still too small to make any significant impact on the rate of progress. The lack of basic research is partially related to the fact that thoughtful and detailed investigations in this field are complicated, time-consuming and expensive and demand considerable experimental ingenuity. The lack of basic research may also be partly due to insufficient motivation for investigators to enter the field.

The reactions which make glow discharge (cold plasma) processes attractive are often dominated by surface phenomena [62] which occur in a very complicated plasma environment. Moreover, the basic information needed to understand these surface processes is usually unavailable from the plasma experiments. The surfaces exposed to the plasma are uncharacterized with respect to their geometrical structure, chemical composition and electronic properties. Past experience in surface science suggests that real understanding will not occur until these parameters are defined. Furthermore, the flux and type of species incident on the surface are almost always unknown. In addition, the flux and energy of ions and/or electrons impinging on a given surface is usually undefined but is known to influence many reactions markedly [63]. This lack of information forces development of industrial processes primarily on the basis of parameter studies and intuition. This is the state of the art. The plasma reactor parameters which are investigated often include pressure, types of gas or gases, flow rates, residence time, r.f. power, fixture geometry, fixture materials, the presence or lack of ion bombardment etc. and

often do not lead to a basic understanding of the physics and chemistry. Because of this complexity and lack of understanding, the processes used by industry are quite probably not optimized and neither is the methodology of process development. Moreover, other useful processes remain undeveloped.

If a body of information were available in a few key areas, this situation would be greatly improved. Some of the key areas involve characterization of the glow discharge while others are related to particle-surface interactions. These areas in which research is needed will now be briefly outlined.

#### 4.1. Concentration of particles in a plasma

Techniques for routinely measuring the concentration of all radicals, ions and stable molecules in a glow discharge are greatly needed. The availability of such techniques would save immense amounts of money in development costs and would also lead to a large increase in knowledge about plasma reactions. Plasma diagnostics using optical techniques, such as laser-induced fluorescence [64–66], optical emission spectroscopy [67], optical absorption spectroscopy [68], actinometry [69] and optical galvanic spectroscopy [70], show some promise of being very useful in this regard. However, quantitative measurements using these optical techniques will require a knowledge of adsorption cross sections and the electronic structure of radicals. This information is frequently unknown. In our opinion, research directed toward making such measurements would be extremely valuable.

The concentrations of particles in a plasma can also be determined with mass spectrometry [38]. Further development of this area would be quite useful, but it probably does not have the same potential for advancing understanding as do the optical techniques. In any case a real understanding of surface processes occurring in a plasma will not be developed until (among other unknown factors) the type and concentration of species in the gas phase can be determined.

#### 4.2. Dissociation in plasmas

Many plasma reactions are initiated by plasma-induced dissociation of stable molecules, and therefore more knowledge of cross sections (and, in particular, dissociation cross

sections and dissociative processes) would be valuable. Some information is available [71–78], but much more is needed. Techniques are available for measuring cross sections but such experiments are complicated and time consuming. Information in this area could be rapidly expanded if competent and interested investigators were encouraged to address this problem.

#### 4.3. Electron energy distributions

For knowledge of dissociation cross sections to be useful, several factors must be known about electron energy distributions in a glow discharge. For example, the dissociation rate in a glow discharge is given by [79]

$$G = \int_V \int_E \rho N(E, V) \sigma_d(E) \left(\frac{2E}{m}\right)^{1/2} dE dV \quad (1)$$

where  $N(E, V)$  is the electron energy distribution,  $\sigma_d(E)$  is the total dissociation cross section,  $\rho$  is the density of undissociated parent molecules and  $V$  is the discharge volume. A 13.56 MHz glow discharge reactor is widely used for a variety of applications; nevertheless, almost no facts are known about the electron energy distributions in these reactors. The present authors are aware of only one attempt to model the electron energy distribution [80] in this type of reactor, and that effort is at present unpublished. It is also possible that the work of Garscadden [81] could be extended to model r.f. discharges. To our knowledge, no experimental work has been done in this area. Another approach to understanding electron energy distributions in a glow discharge may be to develop theoretical models of such systems. We suspect that application of the tools developed to understand laser plasmas could yield much information if they were applied to the types of glow discharge widely used for industrial purposes.

#### 4.4. Plasma potentials

Processes occurring in a glow discharge often depend quite strongly on the plasma potential or, more correctly, on the potential difference between the plasma and a given surface. The potential of the surface is often measured or estimated, but in most applications the plasma potential is unknown, particularly for r.f.-driven plasmas. Some basic information on plasma potentials has been

published [82, 83], but routine estimates or measurements of the plasma potential in the reactor where a given industrial process is being developed are needed. It would be of great advantage to development engineers if a body of basic information was available which would allow an estimate of plasma potentials in a given reactor.

#### 4.5. Ion energy distribution

There are many synergistic effects in a plasma where ion bombardment enhances a chemical reaction [63]. The magnitude of the synergistic effect depends on the energy of the incident ions. Consequently, a body of information about the energy of ions which collide with surfaces in a plasma reactor would be very valuable. This area is amenable to both experimental and theoretical approaches. It is also important to understand the effect of ion bombardment on the characteristics of materials deposited in a plasma environment.

#### 4.6. Plasma-surface interactions

The final key areas involve plasma-surface interactions. Ideally, well-defined surface experiments should be conducted inside a plasma; however, at present this seems to be impossible. Therefore, investigations in these areas should probably be conducted outside the plasma where well-characterized molecular beams can be interacted with well-characterized surfaces. The lack of understanding of plasma-surface interactions is directly attributable to the fact that surface reactions often involve radicals and there are few investigations of the interaction of a flux of radicals with a well-defined surface. Moreover, there are synergistic effects in the plasma.

Basic research in four areas of surface science could do much to remedy this lack of information. These areas include (1) recombination reactions, *i.e.* investigation of reactions at a surface where radicals recombine to form stable molecules, (2) investigation of synergistic effects where ion, electron and photon bombardment change the reaction characteristics of the incident radicals (*e.g.* a knowledge of the dependence of reaction rate constants on the type and energy of bombarding particles would be very useful), (3) investigation of the adsorption characteristics of a number of radicals including a determination of sticking probabilities as a function of

surface coverage and conditions (some sticking probability measurements have been attempted as, for example, is reported in ref. 84) and (4) investigation of mechanisms for the conversion of reactants to products in the surface region. For etching reactions, these experiments could include identification of products on the surface (*e.g.* by using X-ray photoelectron spectroscopy) and identification of products and measurement of energy distributions of particles entering the gas phase, *e.g.* by using modulated beam mass spectrometry. For plasma polymerization, information on growth mechanisms may be the most important area to investigate.

The equipment required for this type of research would probably include a standard ultrahigh vacuum system with the capability for Auger spectroscopy, low energy electron diffraction, UV photoelectron spectroscopy and X-ray photoelectron spectroscopy as well as for ion and electron bombardment. This capability would be used to characterize the sample surface. In addition, two or more well-characterized molecular beams of radicals directed onto the surface would be needed. These molecular beams should be chosen to simulate in the best way a specific plasma of interest. This latter demand is the major experimental problem. It is quite difficult to generate a molecular beam of a given radical which does not contain other radicals or impurities. Nevertheless, it is our opinion that research along the lines suggested above could be quite productive, although it would be expensive and demand considerable ingenuity.

#### 4.7. Characterization of plasma-deposited materials

Finally, the relationship between the reactions which occur in the plasma and at surfaces and the characteristics of deposited films need to be understood. At present, there is very little understanding of this area. Enhanced understanding will require experiments which relate the detailed properties of deposited films to well-characterized surface and plasma reactions.

### 5. THE RELATIONSHIP BETWEEN SCIENCE AND TECHNOLOGY: EXAMPLES

A few problems that could be resolved in the field of plasma etching, if some of the

above information were available, will now be mentioned. Similar examples could be given for other non-equilibrium plasma processes, such as plasma deposition, glow discharge sputtering, plasma oxidation and plasma polymerization.

Let us consider a plasma etching process which uses  $\text{CF}_4$  (gas).  $\text{CF}_4$  itself is quite inert and so the etching reaction results from radicals produced by electron-impact-induced dissociation of  $\text{CF}_4$ . There are three major dissociative processes in  $\text{CF}_4$ , namely dissociative attachment ( $\text{CF}_4 + e \rightarrow \text{CF}_3^- + \text{F}$  or  $\text{CF}_4 + e \rightarrow \text{CF}_3 + \text{F}^-$ ), dissociation into neutral fragments (*e.g.*  $\text{CF}_4 + e \rightarrow \text{CF}_3 + \text{F}$ ) and dissociative ionization (*e.g.*  $e + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F}$ ). The cross section for each of these processes is known or could be estimated. Therefore, if the electron energy distribution was known for a given plasma reactor, then the dominant dissociative process could be determined and hence ways to optimize it sought.

As a second example, the maximum quantity of atomic fluorine available for etching is equal to dissociation rate  $G$  given by eqn. (1). The efficiency of the discharge process could be estimated by comparing the amount of fluorine incorporated into etch products (*e.g.* using mass spectrometry) with the dissociation rate  $G$ . This type of estimate again demands a knowledge of the electron energy distribution and the relevant cross sections.

A third example involves recombination. The importance of recombination reactions (*e.g.*  $\text{CF}_3 + \text{F} \rightarrow \text{CF}_4$ ) could be estimated by comparing  $G$  with the quantity  $N$  of  $\text{CF}_4$  introduced into the reactor and the quantity  $N'$  pumped away from the reactor. If  $G \gg N$ , then recombination is very important. If  $G > N - N'$ , then recombination is still important. From a practical point of view, elimination of recombination reactions should increase the etch rate. Knowing how the rate of recombination is influenced by operating parameters would allow better process control.

In other situations, it may not be necessary to dissociate the molecule in order for etching to occur. The interaction of  $\text{SF}_6$  with silicon may be an example since it has been shown that vibrationally excited  $\text{SF}_6$  will spontaneously react with silicon [85]. Comparison of the dissociation rate with the etch rate could indicate whether dissociation was important for the plasma etching of silicon using  $\text{SF}_6$ .

If the etch rate is much greater than the dissociation rate, then vibrational excitation of  $\text{SF}_6$  may be the dominant process which leads to etching.

Although a large number of examples could be given, we shall use one example which illustrates the importance of knowing (1) the concentration of particles in the gas phase, (2) the reaction probabilities of these particles at a surface and (3) the products formed by recombination and etching reactions. Let us consider the etching of  $\text{SiO}_2$  in a glow discharge which uses  $\text{CF}_4$  (gas). Electron impact dissociation of  $\text{CF}_4$  produces primarily the species  $\text{CF}_3$ ,  $\text{F}$  and  $\text{CF}_3^+$ . Subsequent reactions may produce many other species. A knowledge of rate constants and gas phase concentrations would allow estimation of whether gas phase recombination (*e.g.*  $\text{CF}_3 + \text{F} \rightarrow \text{CF}_4$ ) was a significant loss mechanism for fluorine atoms. A complete lack of information about the gas phase  $\text{CF}_3$  concentration at present prohibits this estimate. In an early paper [86] it was speculated that  $\text{CF}_3$  radicals would spontaneously etch  $\text{SiO}_2$ . Many investigators have subsequently made the same suggestion. This speculation led to the development of one of the key processes in the fabrication of very-large-scale integrated circuits, namely the formation of contact windows. Yet today the true role of  $\text{CF}_3$  radicals is still unknown, and there has been no persuasive experimental verification of the early speculation. A well-defined experiment needs to be conducted to determine whether this reaction actually occurs.

It has been conclusively shown that fluorine atoms react with  $\text{SiO}_2$  and that ion and/or electron bombardment greatly enhances the reaction rate. A knowledge of the gas phase concentration of  $\text{CF}_3$  and fluorine and of their reaction probabilities (sticking probabilities) at the  $\text{SiO}_2$  surface would allow determination of which particle dominates the etching reaction. The presence of ion bombardment is likely to alter these reaction probabilities, *i.e.* there is probably a synergistic effect. Synergistic effects have been investigated for fluorine alone but not for  $\text{CF}_3$ . An investigation of synergistic effects for the interaction of  $\text{CF}_3$  with  $\text{SiO}_2$  under ion bombardment would be very enlightening. The carbon deposited onto the  $\text{SiO}_2$  surface must eventually leave the surface through an etch-

ing or recombination reaction. The products of this reaction are likely to be  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{COF}_2$  or  $\text{CF}_4$ , or a combination of these molecules. Experiments are needed to determine which of these molecules do indeed leave the  $\text{SiO}_2$  surface and how that is affected by ion bombardment. This type of information would also allow estimation of that fraction of the fluorine adsorbed on the surface which is eventually incorporated into an etch product.

Similar examples of fundamental issues which might profitably be addressed in relation to other applications of non-equilibrium plasmas could be given, particularly where plasmas or synergistic effects are involved. Plasma etching is perhaps the most extensively studied area. The amount of fundamental information available on PACVD and the growth of films under energetic particle (ions, electrons or photons) bombardment is small by comparison. Questions pertaining to the constitution of the plasma and how it determines film composition, morphology, stress etc. need to be answered before attempts can be made to minimize the number of parametric adjustments to produce desired film properties. This can be illustrated using PACVD as an example. The development of PACVD has been almost totally empirical. This is of course not surprising in light of the overall complexity of the reaction systems. Nevertheless, progress has been encouraging and the result is that the process has been used in the applications described above. However, there are clearly identifiable research needs. In addition, a more complete understanding of the process would be expected to result in a broader range of applications. Two examples will be given.

The first is in the deposition of silicon nitride passivation coatings. The quality of the

barrier layers is improved as the substrate temperature is increased and the entrapped hydrogen content is decreased. It appears that substrate ion bombardment during deposition yields improved coatings at low substrate temperatures [87]. However, the detailed mechanisms are not understood. Therefore, it is difficult to project the degree of improvement that should be anticipated for the ion bombardment approach. Perhaps other directions would prove to be even more fruitful.

The a-Si:H solar cells provide a dramatic example of a case where a very large pay-off could come from an improved understanding of the PACVD process. The a-Si:H coatings tend to grow in two-phase structures of the form shown schematically in Fig. 10 [88-90]. The columnar grains are composed of a dense amorphous silicon with point defects which are largely passivated because hydrogen has a monohydride bonding configuration. The space between these grains contains a second-phase tissue material of low density amorphous silicon with a considerable density of hydrogen in polyhydride bonding configurations. Coatings deposited at high rates exhibit the two-phase structure on a size scale (10-100 nm) that is clearly visible by scanning and/or transmission electron microscopy [89]. However, under certain deposition conditions the two-phase structure cannot be seen even by transmission electron microscopy, although there is evidence that the general columnar features may exist on a size scale (less than 10 Å) too small to be clearly resolved by transmission electron microscopy [89]. It is this dense apparently single-phase material that yields the high performance a-Si:H solar cells. Unfortunately, the single-phase material has been obtained only at deposition rates in the

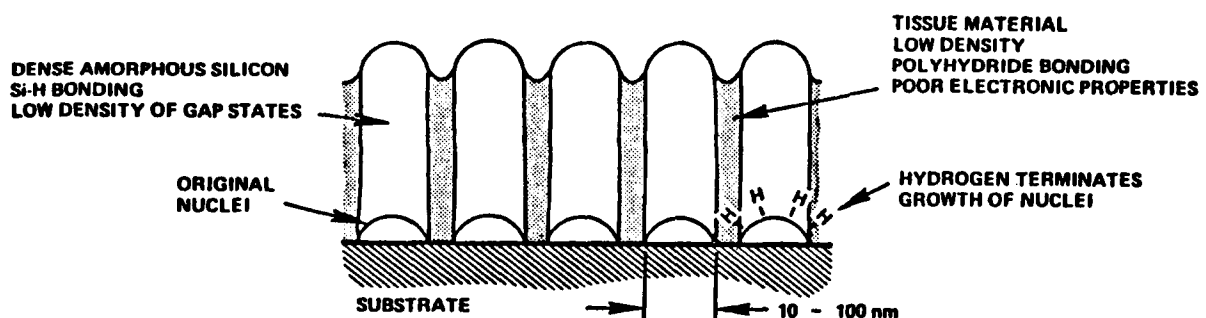


Fig. 10. Growth patterns of amorphous silicon using PACVD.

$1 \text{ \AA s}^{-1}$  range. Considerably higher rates will be required if thin film a-Si:H solar cell modules are to be deposited in the quantity and at the costs that will make them feasible for large-scale photovoltaic applications. Thus, for example, the fabrication of high quality a-Si:H solar cells at a deposition rate exceeding  $10 \text{ \AA s}^{-1}$  is one of the primary tasks in a recent U.S. Department of Energy *Request for Proposals* [91]. Modest ion bombardment during deposition appears to widen the range of conditions in which the high quality material can be deposited [88]. Intense ion bombardment is clearly seen to remove the columnar structure; however, it appears to create other defects which compromise the photovoltaic performance of the material. There is some evidence that the use of an alternative starting material such as  $\text{Si}_2\text{H}_6$  may permit higher deposition rates [92]. However, it is clear that the most prudent approaches and perhaps even the viability of the truly low cost thin film PACVD amorphous silicon solar cells are obscured by the lack of basic understanding of the mechanisms involved.

## 6. CONCLUSION

There are many questions about basic mechanisms (other than those posed above) in plasma processing which remain unanswered despite the fact that these are the most studied reactions. Moreover, many different gases are used for other materials applications, and similar questions arise for these situations. For example, chlorine-based gases are widely used in the semiconductor industry to etch silicon and aluminum. A plasma process for etching copper and magnetic materials, such as nickel and iron, is urgently needed but at present unavailable. Analogous research is needed for an understanding of plasma polymerization, plasma oxidation and PACVD. Therefore, it is certain that basic research directed toward an understanding of relevant plasma reactions will strongly influence future technology development. Basic research in this area is both interesting from a scientific point of view and profitable from an applications point of view. The fields of PACVD, plasma etching and plasma polymerization which involve very complex chemistry are to be contrasted with the fields of glow

discharge sputtering, surface modification, surface cleaning etc. which involve more physical processes. In the latter cases, extensive basic research may not be pivotal to continued development.

Real advances in the understanding of the plasma processes mentioned above require the development of new experimental methods or application of sophisticated techniques from other scientific areas. This situation is reminiscent of the field of surface science in the late 1960s and early 1970s, where the development of low energy electron diffraction, Auger spectroscopy, X-ray photoelectron spectroscopy, UV photoelectron spectroscopy, X-ray extended fine-structure spectroscopy etc. led to a dramatic increase in basic knowledge and had a powerful impact on the development of technologies which hinged on surface phenomena. Financial support for basic research would probably be most effective if given to investigators who are willing to apply new techniques or else to apply tools from the fields of surface science, atomic physics and lasers (or other optical techniques) to the field of plasmas. In our opinion, support for research based on parameter studies is not expeditious unless directed toward the specific development of a product or process.

Finally, the number of experimental parameters which influence the operating characteristics of a plasma processing system is very large. A body of basic information, such as that described above, is needed so that qualitative or semiquantitative estimates can be used to determine the dominant parameters for a particular application. It is not necessary to have a quantitative understanding of the physics and chemistry occurring in each plasma processing system, but it is important to have a qualitative understanding of the composition of the plasma, the reactions which are occurring and the effect of parametric variations on these. Such information would provide, at least, a modicum of predictability and perhaps a more rational basis for process development.

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