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Plasma Processing of Materials

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PLASMA PROCESSING OF MATERIALS

Report of
The Committee on Plasma Processing of Materials

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The report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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ABSTRACT

A National Research Council committee was formed to study recent developments in processing materials through the use of plasma technology. Noteworthy advances in this field have occurred in several foreign countries, and great promise is shown for a number of new and improved methods for materials systems. The study addresses thermal plasma melting and remelting technology, extracting and refining technology, plasma deposition, thermal plasma synthesis and consolidation, and processing using low-pressure nonequilibrium plasmas. Opportunities based on these technologies are discussed, and priorities for support of research and development are suggested.

The committee points out that thermal plasma processing technology in the United States has generally not advanced beyond laboratory-scale or pilot-plant stages. In contrast, large-scale production facilities have been developed in the Soviet Union, the German Democratic Republic, and Japan. Significant advances in some specialized areas have also been achieved in several European countries, Canada, and South Africa. The United States, on the other hand, is at the leading edge of the processing science and technology associated with the application of low pressure plasmas as employed especially in the electronics industry.

The committee concludes that there would be a substantial payoff from funds devoted to research and development, with the most promising being perhaps the area of plasma deposition processing as it relates to microelectronics and very-large-scale integrated circuits. Specific suggestions are given for research and development projects in each of the technologies studied.

PREFACE

Plasma processing of materials is the practical employment of two interrelated disciplines--plasma chemistry and arc technology. Both fields make use of the plasma state of matter, wherein a plasma, made up of a mixture of neutral particles, ions, and electrons, can potentially be utilized for producing new materials with unusual, superior properties, for developing new chemical compounds and processes, and for altering and refining materials and surfaces. This potential, a part of which has already been realized, can play a significant role in the future of materials science and engineering endeavors.

These possibilities have been recognized in several foreign countries, and notably Japan, the Soviet Union, and the German Democratic Republic have taken lead roles in pioneering the exploitation of plasma processing science and technology for their national needs.

With the growing awareness in the United States that plasma processing promises a broad range of new and improved processing operations for materials systems, the Department of Defense and the National Aeronautics and Space Administration requested the National Research Council to study this subject in a broad, fundamental manner. Such a study would assist in organizing the information presently available about the field, in assessing its specific importance to materials science and engineering, and in providing a perspective for future investigations.

The Committee on Plasma Processing of Materials was formed by the National Materials Advisory Board (NMAB) to study the areas of materials science and engineering processing of materials pertinent to:

- The unique aspects of utilizing plasmas for materials processing
- The use of thermal plasma for melting and remelting technology
- The technological opportunities in extractive metallurgy
- Spray deposition for near-net-shape manufacturing
- Thermal plasma synthesis and consolidation (e.g., the production of submicron oxide powders, synthesis of ternary carbides and nitrides, plasma sintering of ceramic materials, and the spheroidization and densification of porous particles and conglomerates)
- The potential for processing materials using low-pressure, nonequilibrium plasmas

The committee was asked to provide an overview of the various technological opportunities in plasma processing and to suggest the kind and extent of research and development necessary to advance plasma processing technology.

In carrying out its assignment the committee examined all technical and scientific aspects of plasma processing. It benefited from the experience of many people engaged in the field, both in the United States and abroad, through examination of their writings and through personal contacts and discussion. Although the committee did not go deeply into the complex legal and economic issues of certain aspects of plasma processing, it was keenly aware of these nontechnical factors.

This report presents the committee's findings based on extensive deliberations during its review and distillation of a large body of information.

ACKNOWLEDGMENTS

The committee wishes to express its appreciation to those who have contributed to this study. In addition to the members and liaison representatives, a number of individuals made substantial contributions to this report. Some of these were professional colleagues of the committee participants who lent their ideas, advice, and assistance to various portions of the work. Others to whom the committee is also grateful are those who gave tutorial presentations to the committee and participated in subsequent discussions. Each provided an overview of some facet of the plasma processing situation that was essential to the committee. In this regard, we wish to acknowledge the contributions of Professor Ken Reid, University of Minnesota; and Dr. Douglas Harris, APS-Materials, Inc., Dayton, Ohio.

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CHAPTER 7

PROCESSING OF MATERIALS USING LOW-PRESSURE, NONEQUILIBRIUM PLASMAS

Low-pressure, low-temperature gas discharges (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 interactions, both physical and chemical, of plasmas with solids and cover a broad spectrum of topics bordering on many disciplines. It is not our intention to provide here an inclusive or exhaustive coverage of the subject matter; instead we will focus on a few applications that illustrate some of the unique abilities of plasmas to modify surfaces and produce end-products with substantial technological and economic significance.

Modifications of solid surfaces arising from interactions with cold plasmas can be broadly classified as follows:

- Surface Cleaning and Alteration--Cold plasmas are used to remove trace contaminants as well as 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 [1] and the treatment of polymers to increase wettability or produce molecular weight changes in near-surface regions [2].
- Chemical Alteration--The chemical composition of surface and near-surface regions can be altered by interactions with plasmas. Oxidizing (e.g., by plasma anodization), nitriding, carbiding, and siliciding of metal or semiconductor surfaces are examples [2].
- Etching--Atom-by-atom removal 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 increasingly becoming indispensable techniques for the fabrication of microelectronic devices, particularly silicon integrated circuits [3].

- Film Deposition--Plasmas are widely used for the deposition of thin films onto surfaces [4]. 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-enhanced chemical vapor deposition, sputter deposition, and ion plating are the more important techniques employed.
- Texturing--Surface topography can be altered by interaction with a plasma. Both etching and deposition are usually involved in texturing.

The plasmas of interest for surface modification are low pressure ("glow") discharges. Operating pressures range from $\sim 10^{-4}$ torr to 10^{+1} torr, depending on the application. These plasmas contain free electrons, positive and negative ions, neutral atoms, and, in the case of molecular gases, neutral molecules and molecular fragments (including free radicals) produced primarily by electron impact dissociation. Average electron energies range from ~ 1 to 10 eV, while the energies of ions and neutrals in the bulk of the plasma are substantially less (~ 0.1 eV). Thus the plasma is effectively "cold" even though the electron energies correspond to temperatures up to 10^5 K. This rather unique nonequilibrium state of affairs makes such discharges particularly suited to a number of applications where technical considerations impose temperature restrictions. For example, the deposition of inorganic films to function as passivating layers in silicon integrated circuits has been carried out almost exclusively by plasma deposition because alternative techniques that can produce films of the requisite quality require temperatures incompatible with circuit metallization [5].

Surface modification results from energy transfer between a plasma and a solid surface. Energy can be transferred by optical radiation (UV photons are particularly important in some of the applications of interest), electron and ion impact, and neutral particle fluxes (free radicals are particularly important in certain applications). The energy is dissipated by a variety of physical and chemical processes, as will become apparent in the following section.

PROCESSES AND APPLICATIONS

In this section we describe several processes for modifying solid surfaces with plasmas that illustrate the various physical and chemical phenomena involved as well as the extremes in the status of present knowledge of the processes from relatively well-understood to relatively poorly understood.

Sputter Deposition of Films

Figure 7-1 shows 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 the case of reactive sputter deposition. A gas is introduced to the vacuum chamber at a pressure ranging from a few millitorr to about 100 mTorr, and a discharge is ignited by applying a dc or rf voltage of sufficient

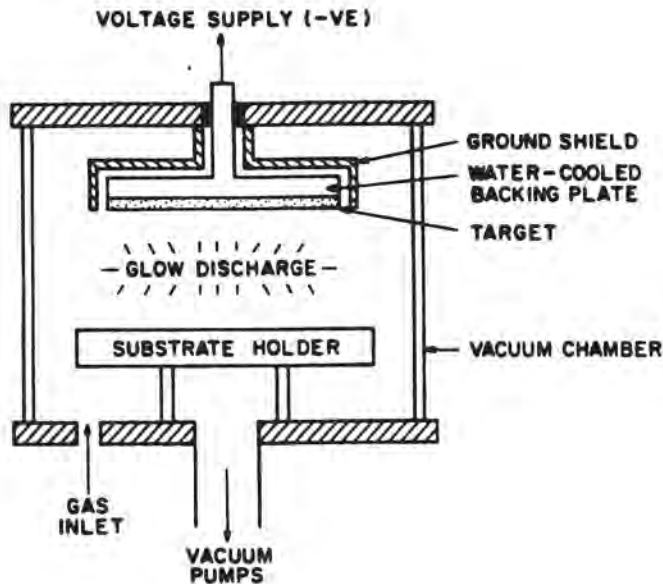


FIGURE 7-1 Cross section of a sputtering system.

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 (≈ 1 cm) sheath between the target and the plasma. Under these conditions, positive ions are drawn from the plasma, are accelerated across the sheath, and strike the target surface. When the arriving ions have energies exceeding a certain threshold value (the sputtering threshold, typically tens of electron volts), they can cause ejection of target atoms as they exchange energy and momentum with the target. The ejected atoms condense on all surfaces 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 keV. 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, TiO_2 films can be deposited by sputtering Ti in O_2 or Ar- O_2 mixture; Si_3N_4 films result when Si is sputtered in N_2 or NH_3 discharges.

In practice, use is often made of magnetic fields to enhance the rate of sputter deposition in what is known as magnetron sputtering. The fields, usually applied by fixed, permanent magnet pole pieces in close proximity to the target, 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 that the number of high-energy

(secondary) electrons reaching the substrate after ejection from the target is diminished. This reduces substrate heating considerably and makes possible the deposition of films onto thermally sensitive substrates, such as plastics, without elaborate means of heat dissipation [6].

Sputter deposition is a relatively well-characterized, well-understood process. It offers certain advantages in comparison to other film-formation techniques. For example, sputtering is applicable to all materials, provided an appropriate target can be fabricated. Furthermore, compounds and multi-element materials can be sputtered and films deposited with the stoichiometry of the target. An additional advantage is that the sputtered atoms arrive at the substrate typically 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 equipment. 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 reach \$300 million per year by 1985.

Sputter Etching

The sputtering phenomenon is also used to remove surface material under conditions quite similar to those 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, and thus the etching is strongly directional (anisotropic). This is particularly pertinent to certain microelectronics applications where etching is used to transfer very fine (micron-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 [7].

On the other hand, sputter etching 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 SiO_2 film to expose shallow junctions in an underlying silicon substrate, without etching away an unacceptable amount of the junctions. Newer techniques, discussed later on, that rely on both physical and chemical interactions via reactive plasmas are preferable in these applications. 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 on the order of one micron in a magnetic NiFe film with a thickness on the order of half of one micron. Up to 4 million such elements may reside on a chip area of about 1 cm². 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 insitu 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 for acceptably low contact resistance.

Ion Plating

Ion plating, as originally conceived, refers to a technique in which an evaporant stream is condensed on a substrate which serves as the cathode in a dc discharge, typically in Ar (Figure 7-2) [8]. 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 implanted in and intermixed with near-surface regions of the substrate, forming a graded interface. This effect leads to superior adhesion and the possibility of forming novel, nonequilibrium "alloys" in the intermixed region.

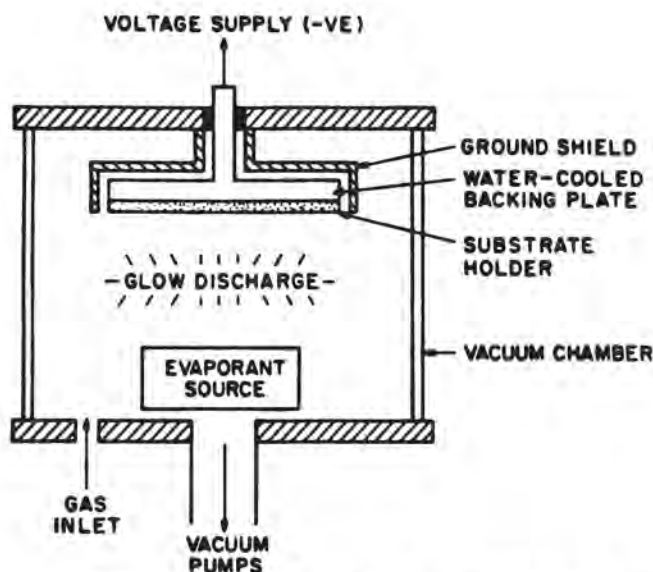


FIGURE 7-2 Cross section of an ion plating system.

Simultaneously, the condensing film is sputter-etched, primarily by argon ions, and some of the sputtered material redeposits on adjacent areas of the substrate that 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" [9]. 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 that have the composition MCrAlY, where M can be almost any element. Similar applications, targeted at protection against wear and corrosion, are found in the electrical connector and fastener industries.

A broader definition of ion plating, advocated by some, includes any film deposition process in which energetic ions bombard the substrate surface during deposition. A subset of this definition is bias sputtering, where a film is sputter-deposited on 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 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 "Ti-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 have a built-in (intrinsic) stress. Built-in stress can limit the practical thickness of a deposited film because the integrated stress results in shear forces that ultimately overcome adhesive forces and produce delamination. It has been observed that the sign (tensile or compressive) and magnitude of built-in 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.

Plasma-Enhanced CVD and Polymerization [10]

The high energies of free electrons in a glow discharge result in impact dissociation of molecular gases. The by-products of dissociation include highly reactive molecular fragments and atoms that readily combine on substrates to form thin solid films. An example, germane to the integrated circuit industry, is the formation of SiN films from plasmas formed in mixtures of SiH₄ and NH₃ or SiH₄ and N₂. Such films can be deposited

at rates of several hundred angstroms per minute at temperatures as low as 250°C. In contrast, thermally-induced reactions between SiH_4 and NH_3 require temperatures in excess of ~700°C to produce SiN . Lower temperatures are desirable to prevent diffusion of shallow junctions and interdiffusion or degradation of metals in silicon integrated circuits.

Polymer deposition can be accomplished with molecular gas plasmas whose parent molecules contain polymerizable structures, such as olefinic double bonds, triple bonds, or cyclic structures. Polymerization is triggered by the formation of reactive species via electron impact dissociation of the parent molecule.

The homogeneity, uniformity, quality, and properties (physical, chemical, and electrical) of plasma-deposited films, whether organic or inorganic, are sensitive to a bewildering number of process variables, such as power, frequency, pressure, flow rate, gas composition, substrate temperature, and reactor geometry, to name only the more obvious. The level of understanding of the effects of these variables is not sufficient for even qualitative predictions to be made. No models of plasma deposition that explain the effects of process variables on film properties have been formulated. Consequently, deposition conditions must be optimized by lengthy and laborious experimentation, and transfer of a process from one apparatus to another is almost never straightforward.

Despite these difficulties, the advantages of plasma deposition, particularly the capability to form films at low temperatures or with unique compositions, have made this approach attractive in several important technologies. Application to integrated circuits has already been mentioned. Plasma deposition as a technique for depositing silicon nitride passivation layers is a routine production process in most of the world's integrated circuit fabrication facilities. Two types of equipment are used in this application. Radial flow reactors (Figure 7-3) were developed first in the early 1970's. More recently, longitudinal reactors (Figure 7-4) resembling "hot wall" low pressure chemical vapor deposition systems have come into use. As might be expected, there is considerable controversy among equipment manufacturers as to the relative merits of each type of system, but neither system appears to have achieved a predominant position among users thus far.

Other integrated circuit applications for plasma deposition, in limited use or under exploration, include the deposition of silicon dioxide, refractory metal silicide, and aluminum films. Competitive techniques, such as physical vapor deposition (evaporation, sputtering, etc.) and low-pressure chemical vapor deposition, may be difficult to displace in these applications because deposition can be accomplished at acceptably low temperatures.

Plasma deposition of inorganic films, such as silicon nitride and silicon dioxide, is also used in other solid-state device technologies, such as GaAs, optoelectronics, and magnetic bubbles. Applications here are primarily for dielectric isolation and passivation.

Another area attracting considerable interest is the plasma deposition of an amorphous form of hydrogenated silicon from a silane plasma for solar cells [11]. This process has potential for developing into a very large industry.

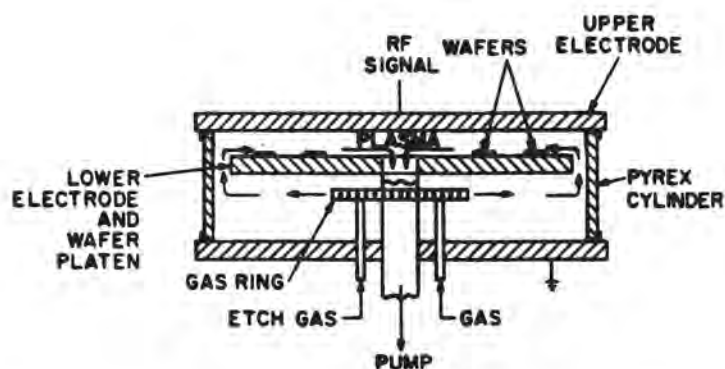


FIGURE 7-3 Cross section of a radial flow reactor.

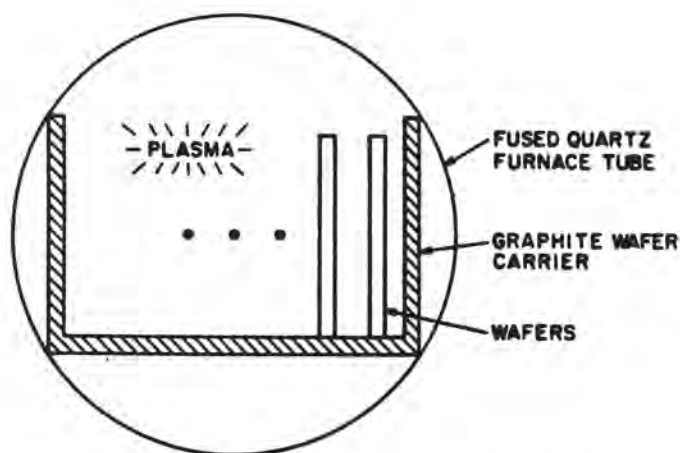


FIGURE 7-4 Cross section of a longitudinal reactor.

The hydrogen incorporated in these films during deposition plays an important role in establishing desirable photovoltaic properties. Numerous Japanese companies have been active in this area. Reported efficiencies have been as high as 10 percent for laboratory devices, but 6 percent for manufactured products is probably a more accurate representation of the state-of-the-art. Solar-powered calculators and watches are among the early products. There is also interest in plasma-deposited amorphous silicon for xerographic and vidicon applications.

Applications for plasma-deposited polymer films appear to be more limited than for inorganic films. Although these films cover substrate topography

reasonably well and can be deposited free of defects and pinholes, even when quite thin, they are generally not mechanically robust and are often semipermeable to environmental contaminants. These shortcomings, together with alternative methods of deposition, may explain the limited application. RCA uses a plasma-deposited styrene film as a capacitive pick-up in its video-disc systems. Plasma polymerized films with low dielectric constants are under exploration for use in integrated circuits as interlevel dielectrics. The low dielectric constants attainable with polymer films are potentially advantageous in reducing parasitic capacitance.

In a quite different area of application, corona discharges are used to modify the surfaces of textiles, effectively functionalizing surface groups in preparation for surface graft polymerization. The grafting can be done by exposing the treated surface to an appropriate plasma containing an effective monomer. Such treatments can be used to change the wettability of the textile surface or to change its printing or dyeing properties.

Polymer membranes for gas separation and water purification can also be formed by plasma deposition, and there are potential applications to biomedical materials.

Plasma-Assisted Etching

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 CF_4 discharge with gaseous SiF_4 as a by-product. The essential chemical reaction is with fluorine atoms generated in the plasma by electron impact dissociation of CF_4 molecules. The development of plasma-assisted etching has been motivated primarily by the needs of silicon integrated circuit technology.

Various methods of 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 (Figure 7-5), a fused quartz cylinder within which an electrodeless rf discharge is maintained. The material to be etched is immersed in the plasma and allowed to float electrically so that only low-energy ions bombard the surface. 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 still 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 \$30,000 for a gross of approximately \$15 million [12].

As the technology evolved, emphasis shifted to parallel electrode systems. In these, the plasma is usually generated by coupling rf power into a gas confined between two parallel electrodes (Figure 7-3) or between a single electrode and a grounded vacuum chamber similar to Figure 7-1. The material to be etched is placed either on the powered or the grounded electrode. The former arrangement is termed reactive ion etching and the latter plasma etching. It soon became apparent that etching in such systems

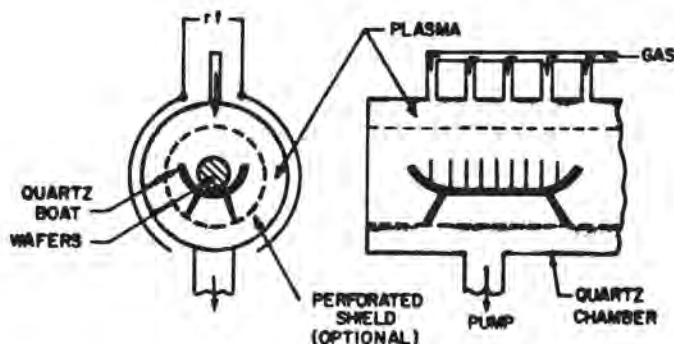


FIGURE 7-5 Barrel reactor.

could be highly directional (anisotropic). Directionality was correlated with the bombardment of the etching surface by energetic ions [13], which, as in sputter etching, impinge on the surface predominantly at normal incidence. The ions are not the primary etchant species but serve, rather, to enhance or even induce reactions between the solid and reactive species generated in the plasma.

Ion-assisted chemical reactions have two important attributes that have had a dramatic 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, because etching occurs through a chemical reaction, etch rate selectivity between different materials can be obtained. This makes possible the patterning of high-aspect-ratio (depth/width) features in a material that 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 256 K dynamic RAM (random access memory), more than a quarter-million bits 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 to 2.0 μm that must be controlled to 0.3 μm 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 marketplace for plasma etching equipment over the past 5 years. At present there are upwards of 60 companies worldwide either manufacturing equipment for plasma-assisted etching or 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 preference, as yet. Thus it is entirely likely that there will be additional entries into a market estimated to reach a quarter of a billion dollars by 1986. Ultimately, however, the equipment market probably will be dominated by a few manufacturers.

The explosive growth, pervasive influence, and strategic importance of integrated circuits (IC's) are well known to all. At the present rate of growth, IC sales will reach \$50 billion annually by 1990. It is fair to say that today's leading-edge IC 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 memory, 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 addressed for the successful application of plasma-assisted etching. For example, in compound semiconductor devices there is an intrinsic difference in reactivity between constituent elements 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 device technologies will be won only through hard-fought empirical battles. This implies significant 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-Perot resonating cavity by reactive ion etching the mirror faces [14-16].

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 [17]. Similar plasma techniques are used to remove a wide variety of organic materials from surfaces; the procedure is often called "plasma-ashing."

STATUS OF SCIENCE BASE

The importance of low-pressure plasma processing of materials is apparent even from the foregoing, 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 United States. The large amount of money and effort expended toward developing plasma technology justifies, in our opinion, a commensurate effort toward understanding the basic physics and chemistry underlying the technology.

As noted earlier, 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, a dearth of knowledge remains. Plasma-assisted etching is a prime illustration of this assertion. While there have been impressive advances in understanding the basic phenomena governing this technology in the past several years [18], significant technological progress has resulted mainly from "hard-nosed" empiricism. In effect, the science has not yet caught up with the technology, or even pointed the way. This is not an unusual situation; indeed, it is characteristic of much of modern technology development, which tends to be evolutionary. However, many of the roadblocks to successful application of nonequilibrium plasma technology could be ameliorated by expanding fundamental knowledge.

It appears at present that the basic worldwide research effort, 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 well-characterized investigations in this field are complicated, time-consuming, expensive, and demand considerable experimental ingenuity; it is also perhaps partially due to insufficient motivation for investigators to enter the field.

The reactions that make glow discharge (cold plasma) processes attractive are often dominated by surface phenomena [19] that 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 upon the surface are almost always unknown. In addition, the flux and energy of ions and/or electrons impinging upon a given surface are usually undefined but are known to strongly influence many reactions [20]. 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 that are investigated often include pressure, types of gas or gases, flow rates, residence time, rf 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.

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 [21-23], optical emission spectroscopy [24], optical absorption spectroscopy [25], actinometry [26], and optical galvanic spectroscopy [27], show some promise of being very useful in this regard. However, quantitative measurements using these optical techniques will require a knowledge of absorption cross sections and the electronic structure of radicals. This information is frequently unknown. Research directed toward obtaining the basic information needed to make them quantitative would be extremely profitable.

The concentrations of particles in a plasma can also be determined with mass spectrometry [13]. 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 happen until (among other things) the types and concentrations of species in the gas phase can be determined.

Dissociation in Plasmas

Many plasma reactions are initiated by plasma-induced (i.e., electron-induced) dissociation of stable molecules, and therefore more knowledge of dissociation cross sections and dissociative processes would be valuable. Some information is available [28-35], but much more is needed. Techniques for measuring dissociation cross sections are available, but they are experimentally demanding and time-consuming. Information in this area could be rapidly expanded if competent and interested investigators were available.

Electron Energy Distributions

To make knowledge of dissociation cross sections useful, one must know something about electron energy distributions in a glow discharge. For example, the dissociation rate in a glow discharge is given by [36]

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

where $N(E, V)$ is the electron energy distribution, $\sigma_d(E)$ the total dissociation cross section, p the density of undissociated parent molecules, and V the discharge volume. A 13.56 MHz glow discharge reactor is widely used for a variety of applications; nevertheless, almost nothing is known about the electron energy distributions in these reactors. The authors are aware of only one attempt to model the electron energy distribution [37] in this type

of reactor, and that effort is, at present, unpublished. It is also possible that the work of Garscadden [38] could be extended to model rf discharges. To our knowledge no experimental work is available. The best approach to understanding electron energy distributions in a glow discharge may be theoretical. We suspect (although we are not certain) that application of the theoretical tools developed to understand fusion plasmas (for example, in Tokamaks) or lasers could yield much information if they were applied to the type of glow discharges widely used for industrial purposes.

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. Some basic information on plasma potentials has been published [39,40], but one needs to routinely estimate or measure the plasma potential in the reactor where a given industrial process is being developed. It would be of great advantage to development engineers if a body of basic information were available that would allow an estimate of plasma potentials in a given reactor.

Ion Energy Distribution

There are many synergistic effects in a plasma where ion bombardment enhances a chemical reaction [20]. The magnitude of the synergistic effect depends on the energy of the incident ions. Consequently, a body of information about the energy of ions that collide with surfaces in a plasma reactor would be very valuable. This area is amenable to both experimental and theoretical approaches.

Plasma-Surface Interactions

The final key areas involve plasma-surface interactions. Ideally, one would like to conduct well-defined surface experiments inside a plasma; however, at present this seems to be impossible. Therefore, investigations in these areas should probably be conducted outside the plasmas, 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 these surface reactions often involve atoms or other types of radicals and that there are few investigations of the interaction of a well-characterized 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:

- Recombination reactions, i.e., investigation of reactions at a surface where radicals recombine to form stable molecules.

- Investigation of synergistic effects where ion, electron, and photon bombardment change the reaction characteristics of the incident radicals. For example, a knowledge of the dependence of reaction rate constants on the type and energy of bombarding particles would be very useful.
- Investigation of the adsorption characteristics of a number of radicals; these should include a determination of sticking probabilities [41] as a function of surface coverage and conditions.
- Investigation of mechanisms for the conversion of reactants to products in the surface region.

In the case of 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).

The equipment required for this type of research would probably include a standard UHV system with Auger, LEED, UPS, and XPS capability, as well as the capability for ion and electron bombardment. This capability would be used to characterize the sample surface. In addition, one would need two or more well-characterized molecular beams of radicals directed onto the surface. These molecular beams should be chosen to best simulate 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 that does not contain other radicals or impurities. Nevertheless, it is our opinion that research along the lines suggested could be quite productive, although it would be expensive and would demand considerable ingenuity.

In the following we give a few of the many possible examples of problems that could be resolved in the field of plasma etching, if some of the information described here were available. Similar examples could be given for other nonequilibrium plasma processes, such as plasma deposition, glow discharge sputtering, plasma anodization, and plasma polymerization, but such examples are not necessary to make the point.

Consider a plasma etching process that uses CF_4 (gas). CF_4 itself is quite inert, so the etching reaction results from radicals produced by electron-impact-induced dissociation of CF_4 . There are three major dissociative processes in CF_4 : dissociative attachment ($\text{CF}_4 + e \rightarrow \text{CF}_3 + \text{F}$ or to $\text{CF}_3 + \text{F}^-$), 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 one could determine the dominant dissociative process and hence seek ways to optimize it.

As a second example, the maximum quantity of atomic fluorine available for etching is equal to the dissociation rate "G" given by Equation 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 CF_4 , introduced into the reactor and the quantity N' pumped away. 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 for etching to occur. The interaction of SF_6 with silicon may be an example since it has been shown that vibrationally excited SF_6 will react spontaneously with silicon [42]. Comparison of the dissociation rate with the etch rate could indicate whether dissociation was important for the plasma etching of silicon using SF_6 . If the etch rate is much greater than the dissociation rate, then vibrational excitation of SF_6 may be the dominant process that leads to etching.

Although a large number of examples could be given, we will use one example which illustrates the importance of knowing (a) the concentrations of particles in the gas phase, (b) the reaction probabilities of these particles at a surface and (c) the products formed by recombination and etching reactions. Let us consider the etching of SiO_2 in a glow discharge that uses CF_4 (gas). Electron impact dissociation of CF_4 produces primarily CF_3 , F and CF_3 . Subsequent reactions may produce many other species. A knowledge of rate constants and gas phase concentrations would allow one to estimate 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 CF_3 concentration presently prohibits this estimate.

An earlier paper [43] speculated that CF_3 radicals would spontaneously etch 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, the formation of contact windows. Yet, today the true role of 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 happens.

It has been shown conclusively that fluorine atoms react with SiO_2 and that ion and/or electron bombardment greatly enhances the reaction rate. A knowledge of the gas phase concentration of CF_3 and F and of their reaction probabilities (sticking probabilities) at the SiO_2 surface would allow one to determine 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 CF_3 . An investigation of synergistic effects for CF_3 interacting with SiO_2 under ion bombardment would be very enlightening.

The carbon deposited on the SiO_2 surface must eventually leave the surface through an etching or recombination reaction. The products of this reaction are likely to be CO_2 , CO , COF_2 , or CF_4 , or a combination of these molecules. Experiments are needed to determine which of these molecules do indeed leave the SiO_2 surface and how that is affected by ion bombardment. This type of information would also allow one to estimate the fraction of the fluorine adsorbed on the surface that is eventually incorporated into an etch product.

Similar examples of fundamental issues that might profitably be addressed in relation to other applications of nonequilibrium plasmas could be given, particularly where reactive plasmas or synergistic effects are involved. Plasma etching is perhaps the most extensively studied area. The amount of fundamental information available on plasma-enhanced CVD and the growth of films under energetic particle (ion, electron, photon) 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 one can hope to minimize the number of parametric adjustments to produce desired film properties.

CONCLUSIONS

There are many questions about basic mechanisms (other than those posed here) in CF_4 - Si , SiO_2 plasma etching that remain unanswered despite the fact that these are the most studied etching reactions. Moreover, many different etching 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 badly needed but presently unavailable. Analogous research is needed for an understanding of plasma polymerization and plasma-enhanced CVD. 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 plasma-enhanced CVD, 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 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 1960's and early 1970's, when the development of "low-energy electron diffraction," "Auger spectroscopy," X-ray photoelectron spectroscopy, ultraviolet 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 that 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 as expeditious unless directed toward the specific development of a product or process.

Finally, the number of experimental parameters that 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 of each plasma processing system, but it is important to have a qualitative understanding of the composition of the plasma, the reactions that 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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