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Plasma Processing in Microelectronics Manufacturing

Plasma processing has emerged as an important technology for the deposition and etching of thin solid films in the manufacture of microelectronic devices. In fact, much of the progress achieved to date in device miniaturization would have been much more difficult without the unique characteristics of plasma processes. It is anticipated that future progress will continue to rely heavily on plasma technology. Although plasma chemical reactors are widely used, a lack of fundamental understanding has resulted in heavy reliance on empiricism in process design and control. The complexities inherent in any chemical reactor are compounded in plasma processing by the presence and active participation of the discharge in both gas phase and surface chemical processes. This has resulted in a technology that is sensitive to many design and operating parameters. A large parameter space gives process engineers flexibility in tailoring process conditions to meet objectives. However, without fundamental insight into the key physical and chemical processes, reactor design and control cannot be based on systematic, rational procedures. The purposes of this review are to introduce chemical engineers to plasma processing practice and phenomenology; to outline the progress made to date in fundamental studies of discharge physics and chemistry; to indicate areas in which chemical engineers must expand their traditional training to participate in plasma processing research; and finally to suggest how established chemical engineering methodology can be applied to plasma chemical reactors.

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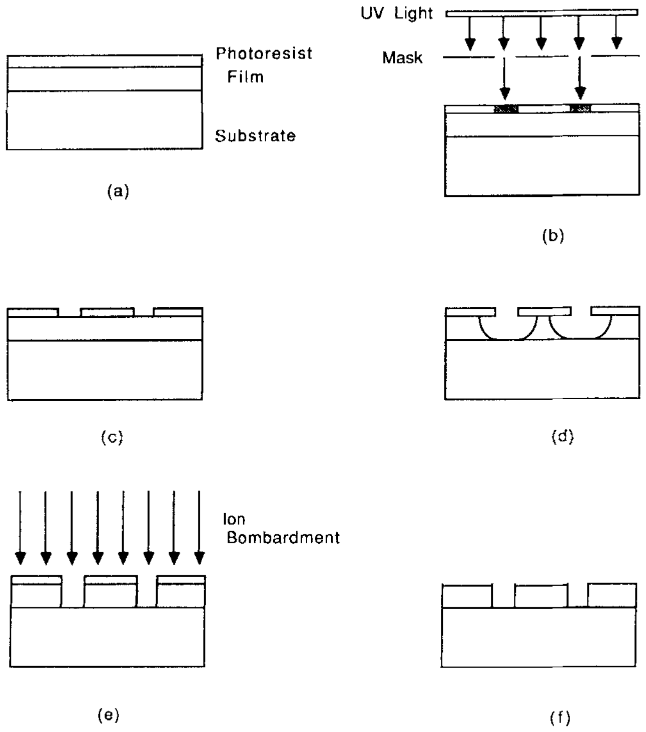
Introduction to Plasma Processing

History, motivation, and future prospects

Molecular gas plasmas are currently widely used in the microelectronics industry for the deposition and etching of thin solid films. Plasma processing is one of many techniques and processes used in the manufacture of integrated circuits (Doane et al., 1982), but the importance of plasma processing to present and future developments in microelectronics, coupled with the growing interest in this technology by chemical engineers, justifies a closer look at industrial practice and the underlying science. Simply stated, microelectronics manufacturing amounts to the growth, patterning, and doping of multiple layers of insulating, semiconducting, and conducting thin films (Hess, 1979). Consequently, deposition and selective etching of films is fundamental to many of the steps involved in this industry. It happens that chemically reacting, weakly ionized gas discharges are particularly powerful tools for depositing and removing thin films.

Plasma etching is the more important process industrially, with VLSI (very large scale integration) relying upon the superior pattern transfer fidelity possible with plasma etching (a more or less equivalent term is reactive-ion etching). The utility of plasmas for etching hinges on their ability, under certain conditions, to remove material in the direction perpendicular to the surface of the film more rapidly than in the direction parallel to the surface. This is known as directional or anisotropic etching and the importance of this characteristic is illustrated in Figure 1. The most common strategy used to pattern thin films is lithography. In this technique, Figure 1a, one begins with a thin film on a substrate. The substrate is usually a silicon wafer, which is typically 0.5 mm thick and 75–200 mm in diameter. The film is coated with a photoresist, which is usually a polymeric material that is light sensitive. The photoresist is exposed



a. Film on substrate is coated with photoresist
b. Ultraviolet light is applied through a mask; exposed regions undergo reactions, while unexposed regions are unchanged
c. Photoresist is developed by removing (or leaving) the portions exposed to light; the next step is to transfer the pattern to the film
d. An isotropic etch results in undercut of the photoresist and poor pattern transfer to the underlying film
e. Anisotropic, or directional etching can occur in plasmas because energetic ion motion is directed toward the surface
f. As a final step, the polymeric photoresist is removed, leaving the desired pattern on the film

Figure 1. Plasma etching.

to ultraviolet light through a mask that allows only certain areas on the coating to be illuminated, Figure 1b. The radiation induces crosslinking or some other reaction to occur in the exposed area so that this portion of the coating will be removed, for example, through rinsing with the appropriate solvent, Figure 1c. Alternatively, the unexposed region could be removed, depending on the resist and development chemistry. The next step is central to our purposes here, because this is where the exposed underlying film is etched, often with a plasma. The goal is to transfer the pattern, which originated with the mask and is now represented by the developed photoresist, to the underlying film. Isotropic etching results in undercutting of the photoresist mask pattern, Figure 1d. The greatest pattern transfer fidelity is achieved when etching occurs *only in the direction perpendicular to the film surface,* Figure 1e, which is known as vertical, directional, or anisotropic etching. Furthermore, the smaller the feature to be etched (or more precisely, the larger the ratio of feature height to width), the greater the importance of directional etching. The last step in the process is to remove the photoresist to leave the desired pattern thin film.

Liquid etchants tend to remove material in all directions with equal efficiency, and as circuit designers continue the quest for ever-smaller devices, the advantages of plasma etching become increasingly apparent. In addition, liquid etchants sometimes cannot penetrate narrow trenches due to surface tension, and the disposal of spent etchant liquids is inconvenient and costly. However, liquid etchants are capable of excellent selectivity (they will etch one material and not another), and the technology is well established, at least in terms of empirical understanding. These advantages notwithstanding, the problems listed above have limited the use of liquids to etching the largest circuit features.

The earliest application of plasmas for etching occurred in the 1960's with the use of oxygen plasmas to remove carbon-containing films from surfaces (e.g., photoresist removal). By the middle of the decade, fluorine- and chlorine-containing discharges were being explored for etching silicon. The first patent describing the use of CF_4 and O_2 mixtures for silicon etching was filed in 1969 and granted in 1971 (Coburn and Winters, 1983). Another important development was the use of plasma-deposited silicon nitride as a passivation (protection) layer for MOS (metal oxide semiconductor) devices. Although plasma-deposited silicon nitride films have many desirable passivation characteristics, there was one problem restricting their use: the extreme conditions required for available liquid etchants to etch windows into the films to allow electrical connections to the underlying device. The problem was solved when it was discovered that CF_4-O_2 plasmas etched these films very well, and use of plasmas for both silicon nitride deposition and etching became commonplace.

Plasmas are increasingly popular for film deposition as well as etching. The two main reasons for using plasmas to deposit thin films are:

1. The plasma-assisted process can usually be done at relatively low temperatures (below 400°C)
2. The films can often be tailored with unusual and desirable properties through the proper manipulation of deposition conditions

Low processing temperatures are desirable because microelectronic devices contain solid state dopants (electrically active material) with carefully defined spatial concentration profiles, and high temperatures will promote solid state diffusion with subsequent degradation of device performance. Also, high temperatures can introduce solid state defects that limit device efficiency.

Most of the important materials used in integrated circuit manufacture can be plasma etched in some gas. The most important applications, not surprisingly, are Si-containing materials: Si, SiO_2, and Si_3N_4. These materials are usually etched in F-containing or Cl-containing gases such as CF_4, C_2F_6, C_3F_8, Cl_2, CCl_4, BCl_3, and others. Plasma etching and polymerization in fluorocarbon discharges has been reviewed by Kay et al. (1980). Metals used primarily as interconnects between devices and between the chip and the outside world include Al, W, Ti, Ta, and their respective silicides (e.g., WSi_2). These are commonly etched in Cl- and Br-containing gases. Polymeric hydrocarbons used for photoresists are often removed in O_2 plasmas. Recent interest in III-V compound semiconductors (e.g., GaAs, InP, and GaP) for faster devices and optoelectronic applications is reflected in a search for suitable plasma etchants for these materials. Some success has been attained using Cl- and Br-containing gases, since group III fluorides are involatile at acceptably low temperatures (less than 300°C). However, a number of difficulties have limited application of plasma etching for III-V processing, usually connected to the differences between the etching characteristics of the two materials (Burton et al., 1984). More detailed lists of etchant gases and materials that have been plasma etched are included in the reviews by Coburn (1982) and Flamm and Donnelly (1981).

Many films of organic polymers, inorganic elemental materials, and compound materials have been grown in plasmas. An alternative is to create radical precursors in a plasma, then transport these radicals in a flowing gas to the growing film, a procedure called downstream processing. An example of this procedure has recently been reported for the deposition of diamondlike carbon films (Robinson, 1986). Perhaps the most important plasma-deposited films include amorphous silicon films used as solar cells, silicon nitride passivation layers, silicon oxide, and oxynitride. Rand (1979), Hollahan and Rosler (1979), Hess (1986), Winters et al. (1985), and Hess and Graves (1988) discuss the application of plasma technology to deposition. Plasma polymerization is reviewed by Bell (1980). The importance of plasma-enhanced chemical vapor deposition for compound semiconductors has been noted by Dautremont-Smith et al. (1988). This is due to the relatively low temperatures required in plasma deposition coupled with the susceptibility of compound semiconductors to thermal degradation.

The future prospects of any technology in an industry as dynamic as microelectronics manufacturing must be treated with caution. It is not possible to say how long a particular process technology will continue to be dominant. However, thoughtful and experienced observers (e.g., Coburn, 1987) suggest that plasma processing will continue to be an important technology in this industry for at least the foreseeable future. Deposition and patterning of thin films will continue to be the primary roles played by plasmas. Plasma deposition may become increasingly important in the future because of the need for low-temperature processes as device dimensions shrink.

There is currently considerable research into the use of laser (Osgood, 1983; Ehrlich and Tsao, 1983; Bauerle, 1986) and ion beam (Kubena et al., 1981; Komuro et al., 1983) technologies to replace plasma processing. Focused beams have the potential advantage of maskless processing since patterning can be provided by directing a tightly focused beam on the wafer in the desired pattern, thereby eliminating the need for lithographic steps. The main disadvantage of beam processing is throughput: tightly focused beams capable of spatial resolution on the order of fractions of microns can process only a small area at a time. The major advantage of plasma processes is that they can provide nearly uniform and large fluxes of ions and radicals to areas on the order of many wafers with inexpensive and simple equipment (all relative to typical beam processes). The major disadvantage of plasma processes is that the plasma is complex and depends on many operating and design parameters, whereas beam systems are usually simpler in operation. The key to the future of plasma processes is improvements in controllability, and this requires a better understanding of plasma physics and chemistry.

Fundamentals of plasma processes

The term "plasma" in this context is used to denote an ionized gas in which the number density of negative and positive charge carriers is nearly equal (Langmuir, 1928). Plasmas vary greatly in their characteristics, ranging from fully ionized, magnetized, and very hot stellar interiors and plasmas used in controlled fusion experiments, to the weakly ionized, cold, nonmagnetized gases used in neon signs and fluorescent lighting fixtures. The plasmas used in microelectronics material processing belong in the latter category. The most striking visual characteristic of these discharges is the emission of visible light, hence the name "glow discharge." Table 1 lists the characteristics of glow discharges. In particular, note that the degree of ionization is very low (fully ionized gases have much different properties), and that electron temperature far exceeds ion or neutral temperature. Most glow discharges are obtained when the gas pressure is in the range of 0.1 to 10^3 Pa (approximately 10^{-3} to 10 torr).

Plasmas used for thin film deposition and etching are sometimes referred to as nonequilibrium discharges because they are far from local thermodynamic equilibrium. A weakly ionized gas is composed of positive and negative ions, electrons, and a large excess of neutral molecules. Deviation from local thermodynamic equilibrium is primarily due to the highly energetic electrons, which are responsible for sustaining the discharge through impact ionization of neutral molecules. Not all electrons in the discharge are sufficiently energetic to ionize neutral molecules, however, since a distribution of electron energy exists. Only electrons in the high-energy tail of the distribution can ionize. These electrons are more efficient at molecular dissociation than ionization, however, so while the degree of ionization is quite low, the degree of dissociation can approach 100% in some cases and 10% is not at all uncommon. This is due to the fact that electron energy necessary for dissociation is typically less than for ionization. The ease with which discharges dissociate molecules into reactive radicals (through electron impact) is the major reason for enhanced chemical reactivity at low gas temperatures. Discharge chemistry is analogous to flame chemistry in that there are many chemically active species interacting simultaneously. As Veprek (1980) points out, due to the highly nonequilibrium nature of low-pressure glows, these systems are capable of "high-temperature chemistry at low temperatures."

The electrically neutral molecular fragments, in addition to undergoing gas phase reactions, can diffuse and convect to surfaces at which they adsorb and react. If the dominant surface reaction products are volatile, the products will desorb (perhaps assisted by ion bombardment), and be pumped away. This is

Table 1. Typical Characteristics of Glow Discharges

1. Number density of electrons and ions	10^8–10^{12} cm^{-3}
2. Fractional degree of ionization	10^{-6}–10^{-4}
3. Electron mean energy	0.1–10 eV (1.6×10^{-20}–1.6×10^{-18} J)
4. Ion and neutral mean energy	0.03–0.05 eV
5. Pressure	10^{-3}–10 torr (0.133–1,333 Pa)
6. Frequency (RF discharges)	50 kHz–50 MHz
7. Electrode separation	1–10 cm
8. Power dissipation	0.01–1 W. cm^{-3}

how surface material is removed in chemical etching. Involatile surface reaction products form films. Hence, the difference between plasma etching and deposition hinges on the nature of the products of surface chemistry.

It should be understood that the species primarily responsible for etching and deposition are neutral—ion flux to surfaces is far too low to account for observed rates of deposition and etching, in contrast to liquid electrochemical systems. However, ions bombarding surfaces play a key role in providing energy for directional or anisotropic etching, which is the most important advantage plasma etching enjoys over other chemical etching processes. The electric fields that form naturally in discharges accelerate positive ions toward surfaces bounding the discharge. These ions can attain energies ranging from a few to hundreds of electron volts, depending on discharge conditions. It has been documented that energetic surface bombardment can have dramatic effects on surface processes. The exact mechanisms of anisotropic etching are unknown, but it is clear that energetic ion motion perpendicular to the surface is closely related to enhanced rates of etching in that direction, Figure 1e. When films are deposited, it has been observed that ion bombardment can alter film properties, so ion bombardment is important in both etching and deposition processes. Winters et al. (1980) and Hess (1986) summarize what is known or suspected about the role of plasma-surface interactions in deposition and etching.

Plasma reactor design and terminology

There are many different modes or types of plasma reactors, and the fact that the terminology for different types is not well defined can cause considerable confusion. Among the terms commonly used to denote some type of gas-discharge-related process are: plasma etching or deposition, reactive ion etching, reactive sputter etching or deposition, and magnetron sputtering. The major distinction among these processes lies in the relative roles of chemical and physical phenomena in the discharge processes. However, it should be realized that there is often some overlap when these terms are used by different authors.

Sputter deposition is a purely physical gas discharge process in which one electrode (the cathode) acts as a target and another electrode acts as a substrate (Chapman, 1980; Townsend et al., 1976). The target cathode is subject to intense positive ion bombardment, and these ions remove material from the target through a momentum transfer ("sandblasting") process. Some of these sputtered atoms find their way to the substrate and condense there, resulting in a deposited film. Other atoms backscatter and redeposit at the target, but sputtering systems are designed to operate at low pressures (on the order of 1–10 Pa) so that this backscattering is minimized, and also so that the ions bombarding the target are not impeded by collisions with gas molecules. Although sputtering is usually a deposition process, it is sometimes used as an etching process, in which the goal is to *remove* material from a substrate. By adding a reactive gas to the system, reactive sputtering is said to occur. The common picture of this process involves chemical reaction between sputtered atoms (e.g., Si) and the reactive gas (e.g., O_2 or N_2), which results in a film deposited at the substrate with a composition different from the target (SiO_2 or Si_3N_4, respectively).

Sometimes a magnetic field is applied to intensify the discharge, and these are known as magnetron discharges (Chapman, 1980). The magnetic field helps to confine electrons, decreasing the rate of loss of the charged species to boundaries. Since a self-sustained discharge requires that the rate of ionization and the rate of loss of charged particles be equal, by lowering the loss rate the discharge can be sustained at lower pressure. When the gas pressure becomes so low that electrons rarely collide with a gas molecule before being lost at a boundary, the discharge extinguishes.

The term "reactive ion etching" is typically used to denote a system in which pressure is relatively low (10–30 Pa) and power high, and means that wafers are placed on the smaller electrode where ion bombardment is usually the highest (Oehrlein, 1986a). (The relationship of electrode size, plasma and electrode potentials, and ion bombardment has been discussed by Kohler et al., 1985a, b). "Plasma etching" usually refers to operation under conditions such that ion bombardment is less intense than in reactive ion etching.

Plasma chemical reactors are relatively simple, as shown in Figure 2. Since these are vacuum systems, some form of vacuum pump (typically a mechanical rotary vane pump or Roots blower) is used, the gas flow is controlled via mass flow controllers, and reactor pressure is controlled independently by an exhaust valve. In order to strike and maintain a discharge, electrical power is applied in the form of a voltage at one electrode; the other, typically grounded, electrode completes the circuit. If the reactor chamber is conducting, it is also grounded. The means of sustaining the discharge varies, ranging from direct current to microwave. The most common approach is to use radio frequency (RF) power at 13.56 MHz (an industry standard reflecting FCC regulations); "RF discharge" typically means the frequency is between about 50 kHz and 20 MHz. Much below 50 kHz, the discharge becomes an intermittent DC discharge, and frequencies in the gigahertz range are referred to as microwave discharges.

There are basically two types of reactor configurations used in plasma processing: the barrel reactor and the parallel plate electrode reactor. A parallel plate electrode arrangement is illustrated in Figure 2, in which the wafers (or wafer for a single-wafer system) are placed on one of the electrodes, which may be heated or cooled. Wafers are subject to ion bombardment in this design, the intensity of which depends on electrode and plasma voltages and gas pressure. In the barrel reactor, Figure 3, wafers are placed on a rack inside a perforated metal shield that forms one of the electrodes in the system. A dis-

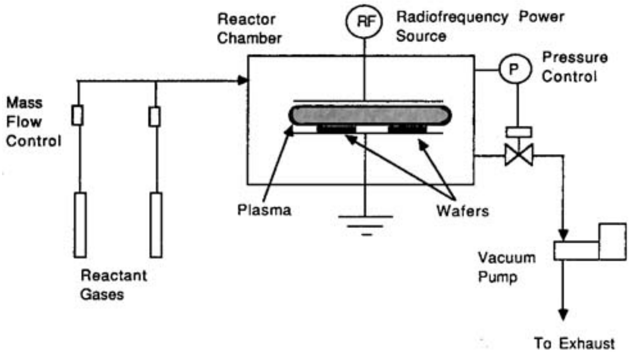


Figure 2. Parallel plate plasma reactor with wafers placed on grounded electrode and plasma filling space between electrodes.

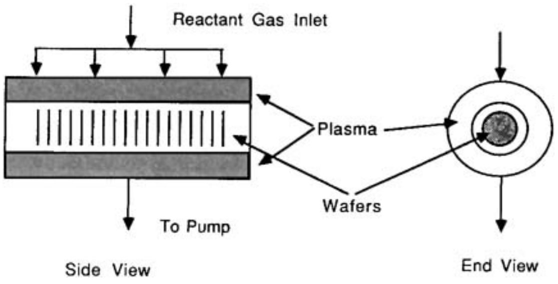


Figure 3. Barrel reactor, in which wafers are placed inside an etch tunnel and plasma is restricted to the outer annulus.

Neutral radicals diffuse to wafers in the absence of ions

charge is struck between this electrode and an outer electrode, and the creation of chemically active radicals occurs in this annulus. Radicals are much longer lived than ions (which recombine quickly outside the discharge) so primarily radicals rather than ions diffuse into the etch tunnel and react with the wafer surface. The lack of energetic ion bombardment precludes anisotropic etching, so the barrel reactor is used more for photoresist stripping and other processes in which directional etching is not necessary.

The conventional view of plasma processes is that surface processes are controlled by the combined action of neutral radicals and molecules adsorbed at the surface and the energy from directed ions. In order to predict the effects of design and operating parameters on plasma reactor performance, one thinks in terms of the effects of these changes on the flux and composition of radicals and the flux and energy of ions at surfaces. The greater the radical flux, the greater the rate of etching or deposition. Higher ion energy and flux tends to correspond to greater etch anisotropy. In the case of film deposition, film microstructure, surface morphology, adhesion, and stress are all functions of ion bombardment.

Process objectives

The first requirement for a plasma etching application is sufficiently high volatility of the reaction product at the surface of the material to be etched. For example, silicon can be etched with fluorine- or chlorine-containing precursors such as CF_4 or Cl_2 to form SiF_4 or $SiCl_4$, respectively, both of which have relatively high vapor pressures. Aluminum (which is commonly used as a conducting interconnect in microelectronics and is therefore an important material) cannot be etched with fluorine-containing gases because the aluminum fluoride (AlF_3) is not sufficiently volatile. If AlF_3 is formed at a surface, further reaction is blocked and etching terminates. Other important etch process requirements include acceptably high etch rates, selectivity, anisotropy, uniformity, smooth surface morphology, no residual material on the surface, and minimal damage to the underlying material from ion bombardment. In deposition, process objectives include high rates at relatively low temperatures, good mechanical properties such as minimal stress and good adhesion to the underlying substrate, conformal coverage of steps, and stability to subsequent processing. In addition, film composition and electrooptical properties are of considerable interest.

Selectivity in etching is characterized by the ratio of the etch rate of the target material to the etch rate of other materials such as the mask or the underlying substrate. Selectivity is usually attained in plasma etching through proper selection of chemistry: some species will etch only the desired material at appreciable rates. However, achieving high selectivity tends (but not always) to come at the expense of anisotropy. This is because high anisotropy usually implies energetic ion bombardment, but ion bombardment induced etching tends to be less selective than chemical etching. One of the reasons plasma etching has been so successful is that a satisfactory compromise between these objectives can be found by exploring parameter space (adjusting, for example, pressure, frequency, and gas composition). An exception to this rule occurs under some conditions when H_2 is added to CF_4 in Si/SiO_2 etching. In this case, increases in both anisotropy and selectivity occur due to changes in plasma chemistry. This is discussed in a later section.

Uniformity means that the etch or deposition rates are the same within the wafer and from wafer to wafer. This is obviously necessary when an entire batch of wafers is processed simultaneously: the sequence of process steps must be the same for all wafers at all times to maximize process yield. In order to achieve uniformity, process designers strive to maintain a uniform flux of radicals and ions on all surfaces to be processed. Once again, this is achieved in practice by trial and error manipulation of process parameters.

Etch residues (undesired traces of material left on the wafer after etching) can cause serious problems because of the possibility of subsequent reactions. For example, a classic problem of etch residues is encountered in etching aluminum with chlorine-containing gases. If all the residual chlorine is not removed from the surface, serious corrosion problems from the formation of HCl can occur when the surface is exposed to water vapor in ambient air.

Damage to underlying material from ion bombardment during etching is one of the most important practical problems in plasma etching. (There has also been some discussion of the deletrious role played by energetic ultraviolet photons, (as by Ephrath, 1982). The greater the anisotropy desired, the greater the ion bombardment flux and energy required. Damage can occur in two ways: ion-induced displacement of lattice atoms and implantation of surface residual material (Oehrlein, 1986b). Both effects lead to modifications in the electrical properties of underlying material. Given the extreme sensitivity of device performance to such alterations, these effects must be closely monitored. When counting the disadvantages of plasma processes, radiation damage is often high on the list.

Stress and adhesion are important considerations in thin film deposition. Films are often deposited with intrinsic stresses and different thermal expansion coefficients between the film and the underlying substrate can cause additional stress. Excess tensile stress in particular may lead to delamination and loss of adhesion: films will peel and crack. The dependence of film mechanical properties on deposition conditions is, once again, poorly understood and very important. It has been observed that ion bombardment can influence film material properties, presumably through inducing changes in lattice atom positions, promoting interfacial mixing, and so on. A recent study of the dependence of stress in plasma-deposited silicon nitride and oxynitride films emphasizes the role of ion bombardment and surface temperature in controlling the rate of hydrogen desorption from the films (Claassen, 1987).

Elementary Reactor Analysis

Loading

Plasma chemical reactors share many features with more conventional chemical reactors, and it is not unusual to find that a chemical reaction engineering principle has been rediscovered by workers in plasma processing. One example of this is the role of flow rate, reaction rate, and residence time on plasma reactor behavior. It had been observed that etch rate under some conditions would decrease dramatically when a large number of wafers were placed in a reactor, a phenomenon termed "loading." It was also observed that etch rates depend sensitively on flow rate through the reactor whenever the reactor is heavily loaded. The major practical difficulty associated with loading occurs near the end of an etch cycle when almost all of the film to be etched has been removed. When the film is nearly gone, the etch rate increases dramatically and it is very difficult to stop etching before considerable overetching occurs. The major problem with overetching is substantial undercutting.

The cause of this behavior was determined to be a high rate of consumption of etchant species (e.g., F atoms) by the film to be etched in the reactor. If the etchant is largely depleted by surface reaction, then etching is reactant-limited and small increases in flow rate correspond to relatively large increases in etch rate. Furthermore, as the etchable film surface area decreases rapidly near the end of the etch cycle, the concentration of etchant increases and etching accelerates. This situation can be easily analyzed (with the aid of several simplifying assumptions concerning the plasma behavior) using elementary reaction engineering principles (Flamm et al., 1982). One solution for loading problems in production reactors is to operate at higher flow rates to increase etchant concentration. The major loss process becomes pumping rather than surface reaction, so changes in the surface reaction rate near the end of the run do not appreciably affect the etchant concentration. Another option is to use electrode materials that etch and thus will consume at least as much etchant as the film to be etched. This has the effect of stabilizing the etchant concentration as a function of time in the etch cycle and thereby reduces the rapid rise in etch rate near the etch endpoint.

Stoichiometry: the etchant-unsaturate model and F/C ratio model

Manipulation of etching characteristics through selection of reactant gas inlet composition has had considerable, albeit qualitative, success. The etchant-unsaturate model of Flamm and Donnelly (1981) and the fluorine to carbon (F/C) ratio concept of Coburn and Winters (1979) are rather similar in that both rely on essentially stoichiometric arguments. In both models of the active plasma chemistry, it is assumed that the etchant is largely atomic radicals, and that mixtures which serve to increase the concentration of these species will increase etch rates; mixtures which serve to promote their recombination into less active species will reduce etching. In a fluorocarbon plasma (e.g., CF_4), the most active etchant is F radicals; these are lost through etching reactions at surfaces and through gas phase recombination reactions with (primarily) CF_3 radicals (Plumb and Ryan, 1986a). In addition, CF_x species can form fluorocarbon films at surfaces, blocking silicon etching. If additives are used in the inlet gas mixture which reduce the concentration of the unsaturated species or decrease the ratio of carbon to active fluorine, then the etch rate will increase according to the models. This is precisely what is observed when O_2 is added to the discharge: CF_x molecules are converted to CO, CO_2, COF, COF_2, and so on. The result is an increase in F atom concentration and an increase in etch rate. On the other hand, if an F atom scavenger is used (the most important is H_2, which will form HF), then the opposite effect occurs: CF_x species concentration increases, fluorocarbon films tend to form on silicon surfaces, F atom concentration declines, and silicon etch rate decreases.

The addition of H_2 may seem like an undesirable strategy, but it is often used when the goal is to etch SiO_2 films selectively over Si films. In this case, the Si film is blocked by adsorbed fluorocarbon and relatively few F atoms are available for etching Si. However, the SiO_2 surface has a ready supply of O atoms to react with adsorbed carbon to form volatile CO or CO_2 and the fluorine reacts with silicon to form volatile SiF_4 (minor species include SiF_2 and $SiOF_6$). Similar behavior is observed in chlorocarbon (e.g., CCl_4) gases. The review of Flamm and Donnelly (1981) on the design of plasma etchants contains extensive discussions of what has been learned about the manipulation of chemistry to achieve desired etch process characteristics.

Coupled with neutral species chemistry at surfaces is the ubiquitous ion bombardment. Halocarbon films tend to be sputtered by ion bombardment, so under conditions that favor ion bombardment (low pressure, high power, and low-frequency applied voltage), halocarbon surface polymerization is decreased. In fact, the combination of polymerized films and ion bombardment has been postulated as a mechanism for anisotropic etching, Figure 4. The idea is that polymerized films form on all surfaces, including the sidewall of the trench to be etched. However, ion bombardment removes this film preferentially at the bottom of the trench due to highly directional ion motion. This continuously clears the bottom of the trench for attack by etchant species, in addition to providing energy for the etching surface chemistry; sidewalls, by contrast, etch at a reduced rate due to coverage of the film. It should be pointed out that a detailed, mechanistic description of the events at an etching surface is still mostly speculation since it is difficult to measure surface species under realistic conditions.

Chemical reaction engineering models

In order to model a plasma chemical reactor, it is necessary to include three basic elements:

1. Electron-impact dissociation of the relatively inert inlet gases into chemically active neutral species
2. Transport and gas phase reaction of these neutral species within the reactor
3. Adsorption, surface reaction, and desorption of products, including the effects of ion bombardment

These processes are typically functions of position in the reactor, and if a radio frequency voltage is used to power the discharge (as is commonly the case) then at least some of the processes will be time-periodic. It is due to the complexity of the three steps listed above that reactor models have so far been fairly rudimentary. Step 2, transport and gas phase reaction, has been treated with the most detail in reactor models to date. Indeed, there is essentially no difference between a plasma reactor and any other kind of reactor in the treatment of neutral transport and gas phase chemistry, so relatively straightforward applications of known principles can be applied to this part of the problem.

Steps 1 and 3 involve discharge physics and surface chemistry and physics, areas that are not at all well understood at present, and which are topics of current fundamental research. These are discussed in some detail in following sections of this paper.

Work on applying reaction engineering principles to plasma reactors was initiated by Bell and coworkers through a series of influential papers: Bell (1970), Bell (1974), Bell and Kwong (1972, 1973), Brown and Bell (1974a, b), Kobayashi et al. (1976) and Jensen et al. (1983a, b). Perhaps the major contribution of this work was the demonstration that chemical reaction engineering theory could be applied to plasma reactors, culminating in the comprehensive treatment of ethane plasma polymerization by Jensen et al. (1983a, b). In the first of two papers, measurements were reported of polymer deposition rate as a function of axial position (using a movable quartz crystal microbalance) and reactor effluent composition measurements using a gas chromatograph. Effluent composition, deposition rate, and the shape of the axial deposition rate profile were found to be strongly affected by variations in discharge power, gas pressure, and residence time in the plasma. The second paper contained a detailed model of transport and chemistry in the reactor, with 11 adjustable parameters to characterize unknown electron-impact dissociation rates, surface reaction rate, and sticking coefficients. Care was taken to demonstrate that the value of these fitted parameters and their dependence on reactor conditions was consistent with known physics and chemistry.

There has been an increase in plasma chemical reactor modeling activity in recent years. A representative but not exhaustive list of recent papers includes: Anderson et al. (1986), Kline (1986), Partlow and Kline (1986), Stenger and Akiki (1986), Kushner (1982; 1986), Edelson and Flamm (1984), Greenberg and Verdeyen (1985), Tachibana et al. (1984), Mocella et al. (1986), Rhee and Szekely (1986), and Dalvie et al. (1986). Progress continues to be made in applying reaction engineering principles to plasma reactors (for example, Rhee and Szekely, 1986, and Dalvie et al., 1986, solve for the neutral gas velocity profile in two spatial dimensions), but major advances in the field will require a much better understanding of discharge physics and plasma-surface interactions. The remainder of this paper will focus on these key topics and the diagnostic and modeling tools being developed and applied to them.

Discharge Physics

Introduction

The foundation for all plasma processes lies in discharge physics. This is because it is through the action of electrons that gas phase chemistry is initiated, and through the action of ion bombardment at surfaces that many of the unique and useful characteristics of plasma processes are realized. Electrons and ions gain the energy necessary for these processes through the action of the electric field. Furthermore, the spatial and temporal variation of the electric field is determined by both the applied voltage at boundaries and the distribution of charged particle number densities. Even inert gas discharges, in which chemistry is essentially nonexistent, are not well understood at present under conditions of interest. The discussion in this section will focus on electrical and physical aspects of gas discharges, ignoring for the moment gas phase and surface chemistry.

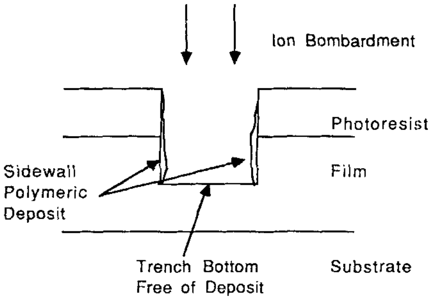


Figure 4. Role of polymeric films in promoting anisotropic etching.

Polymer forms on all surfaces but is removed preferentially at trench bottom

The first requirement of a steady, sustained discharge is that the volume- and time-averaged rate of creation of charged particles be equal to their global rate of loss. If the discharge is sustained through energy imparted to charged particles from an applied electric field, then the discharge is said to be self-sustained. Nonself-sustained discharges would be those whose ionization is provided by application of some external ionization source such as an electron beam or high-energy photons. Plasmas are sometimes said to be "ignited" when operating or "extinguished" when not operating; in fact, this is one example of the similarity between flames and plasmas. In both cases the generally abrupt transition between "on" and "off" states is related to strong nonlinearities in rates of creation and loss processes. This is discussed later in the context of discharge stability.

Discharges of interest in electronic materials processing are weakly ionized, so electrons and ions collide predominately with neutral species. Charged-charged interactions are longer range than charged-neutral interactions: Coulomb potentials vary inversely with separation whereas charged-neutral interactions vary roughly as the inverse fourth or fifth power of separation. This means a single charged particle "feels" the charge of many other charged particles at once, although this effect is reduced by the tendency of the plasma to screen isolated charges. The governing Maxwell equation (under most conditions of interest) is Poisson's equation, which is simply Coulomb's law generalized to continuous charge distributions (Reitz et al., 1980). This implies that the electromagnetic field is quasistatic (Haas, 1973), which turns out to be a good approximation as long as the field frequency is below microwave frequencies (on the order of a gigahertz and above). Except for microwave discharges, which are occasionally used in plasma processing but will not be discussed here, this condition is satisfied and Poisson's equation works well.

The history of gas discharge studies is fascinating both because of the fact that it spans several centuries and because of the important role early gas discharge investigations played in the development of modern physics. Much of the study related to gas discharges has focused on the behavior of individual particles and their collision properties. It is instructive to consider the view of Langmuir:

> Progress in physics during the last 20 to 30 years has been characterized by the remarkable advance in our knowledge of electrons, ions, atoms, and molecules as *individuals*. . . . We now wish to consider how these *processes*, characteristic for the most part of individual electrons, ions or atoms, cooperate to deter-

> mine the *phenomena* of electric discharges. We shall have to deal with the *collective behavior* of these charged and uncharged particles. This field of study in recent years has not received attention comparable to that devoted to the individual particle. The *time seems now ripe to apply all this new knowledge in a systematic* manner to a study of discharges (Langmuir and Compton, 1931)

In fact, study of the collective behavior of the entire discharge continued to lag behind the study of individual collision processes. Several reasons account for this: first, interest in classical gas discharges waned and much attention focused on plasma fusion, magnetohydrodynamics, and space plasmas; second, detailed measurements of fundamental quantities in discharges are difficult, and without measurements to compare with model results, detailed modeling is infertile; and finally, the computational problems associated with solving discharge equations are considerable. It is only recently that the use of low-pressure gas discharges in electronic materials processing has supplied considerable motivation for understanding discharge physics and chemistry. Furthermore, discharge diagnostics and modern computers have become more powerful. As a result, the future of fundamental investigations of low-pressure discharge global structure seems bright, but work combining these powerful tools is just beginning in earnest.

Elementary discharge properties

In order to introduce features common to many discharges, consider a nonself-sustained discharge between infinite parallel plate electrodes, illustrated in Figure 5. We will assume that a steady, spatially uniform, externally applied ionizing source is maintaining the discharge (for example, high-energy photons). Both electrodes are assumed to be conducting and grounded in this example; however, it is straightforward to extend the example to the case in which a voltage is applied between the electrodes. The goal is to predict the electron and positive ion density profiles, the electric field strength profile as a function of the strength of the ionization source. This situation would exist in a photoionization chamber, or the ionization could be supplied by a flame between the electrodes. This highly simplified example is chosen to illustrate some of the basic principles involved in discharge structure.

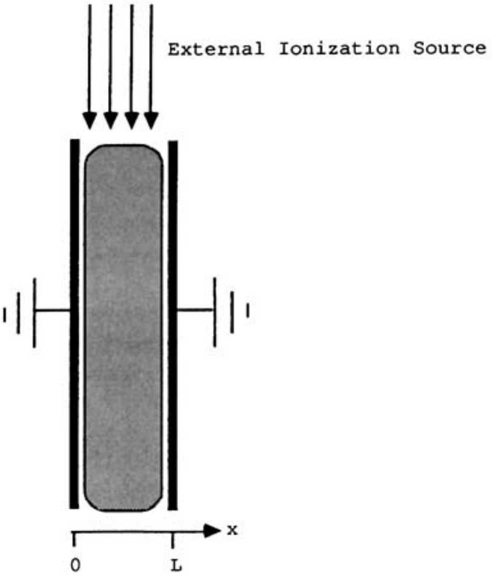


Figure 5. Simple discharge in which electron-ion pairs are created by a uniform, constant ionization source such as an electron or photon beam.

The situation discussed here has been treated by several authors (Wardlaw and Cohen, 1973; Lowke and Davies, 1978). In addition, this system is similar to the positive column of a DC discharge (Allis and Rose, 1954). We will consider the case in which the rate of external ionization is sufficiently strong that ambipolar diffusion controls the loss of charged species. In addition, the gas pressure will be assumed sufficiently high that a continuum analysis is valid. The latter assumption implies that the motion of the charged particles is dominated by collisions with neutral species, which simplifies the expressions governing particle velocity. Since infinitely wide electrodes are assumed, quantities vary only with position between the electrodes and the analysis is quasi one-dimensional. It should be noted that even for this relatively simple example there are many subtleties that space and scope do not permit us to explore. The interested reader may examine the references listed above and references therein.

Equations describing the discharge structure include continuity equations for electrons and positive ions, and Poisson's equation for the self-consistent electric field. Negative ions are assumed not to form in significant quantities, although they could be included by adding another continuity equation. At steady state, the equations take the following form:

$$dj_e/dx = d/dx(-D_e dn_e/dx - \mu_e n_e E) = R_{ionization} \quad (1)$$

$$dj_+/dx = d/dx(-D_+ dn_e/dx + \mu_+ n_+ E) = R_{ionization} \quad (2)$$

$$dE/dx = -d^2V/dx^2 = e/\epsilon_0(n_+ - n_e) \quad (3)$$

Equation 1 is the electron continuity equation, and Eq. 2 is the positive ion continuity equation, with analogous terms. Of course, whenever an electron is created through ionization, a positive ion is also created, so the source term for both equations is the same. Volume loss terms are neglected, which implies that the rate of gas phase recombination of electrons with positive ions is assumed to be small compared with diffusion to the wall and recombination there. Equation 3 is Poisson's equation, which can be expressed either in terms of the divergence of the electric field strength E or the Laplacian of the voltage (potential) V. By definition, the negative gradient of the potential V is the field E. Equations 1 and 2 show that the flux of electrons and ions is due to two terms: a diffusion term and a drift term. The values for corresponding transport coefficients are listed in Table 2; electron diffusivity D_e and mobility μ_e are typically much larger than the positive ion quantities because of the smaller electron mass and higher electron thermal energy. Motion of the neutral gas is almost always negligible as far as charged particle motion is concerned (at least for subsonic neutral flows) because electron and ion net velocities are usually much higher than neutral gas velocity. The fact that electron and ion number density is very low compared to neutral gas density makes the effect of charged particle motion on neutral flow insignificant. For weakly ionized gases, as mentioned before, the ratio of charged particles to neutral particles is on the order of 10^{-4} to 10^{-6}. The neutral gas acts as an essentially stationary, porous matrix through which electrons and ions flow.

Table 2. Parameters for Externally Sustained Discharge

Parameter	Value
Electron difusivity, D_e	$10^6\ \mathrm{cm^2/s}$
Electron mobility, μ_e	$10^6\ \mathrm{cm^2/V \cdot s}$
Ion diffusivity, D_+	$10^2\ \mathrm{cm^2/s}$
Ion mobility, μ_+	$4 \times 10^3\ \mathrm{cm^2/V \cdot s}$
Ionization rate, R_i	$3.3 \times 10^3\ \mathrm{s^{-1}}$

Boundary conditions for Eqs. 1–3 are:

$$n_e = dn_+/dx = V = 0 \quad \text{at } x = 0, L \qquad (4)$$

The separation between electrodes is L, and both electrodes are grounded. Zero electron density at each electrode implies that the rate of recombination at the conducting surface is much faster than the transport processes bringing electrons to the surface. A zero density gradient boundary condition is used for ions rather than zero density as for electrons. This is related to the fact that the ratio of ion mobility to ion diffusivity (which may be expressed as a Peclet number) is a large number compared to the corresponding ratio for electrons. As a result, very thin ion density boundary layers will form in the solution if the zero density boundary condition is used. We are, in effect, neglecting the "inner" solution in favor of the "outer" solution with this boundary condition. For a more complete discussion, the reader is referred to Graves and Jensen (1986). For self-sustained discharges, these boundary conditions (and Eqs. 1–3 also) may be different, but the present set serves as a good introduction. The structure of this relatively simple discharge is a consequence of the creation of charged particles, the space charge electric fields created by these particles, and the transport of the particles to boundaries.

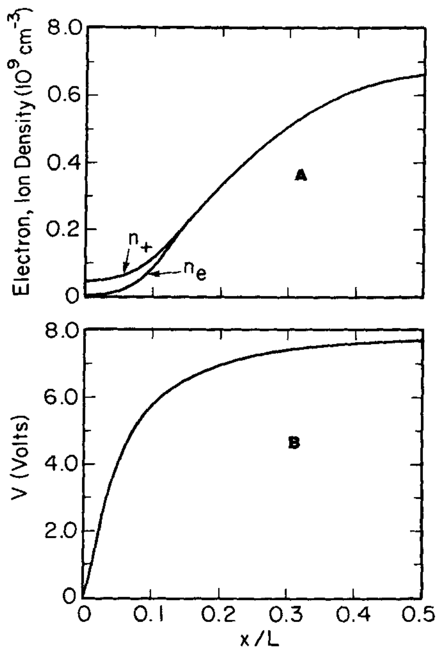
Analytical solutions to Eqs. 1–4 are not possible (due to the nonlinearity in the drift terms), although matched asymptotics have been used to construct approximate solutions (Wardlaw and Cohen, 1973). Using a similar set of equations, Lowke and Davies (1978) obtained solutions numerically. The basic structure of the solution is plotted in Figures 6a (electron and ion density profiles) and 6b (voltage and field profiles) for a sufficiently high ionization rate. Parameters for the simulation are listed in Table 2. The central region between electrodes is quasineutral, meaning that electron and ion number densities are almost equal. From Eq. 3, we see that this corresponds to a nearly zero slope electric field, and it turns out that the value of the field is near zero. Due to symmetry, the electric field goes through zero at the center of the gap, the electron and ion densities are exactly equal there, and the charged particle flux is zero. By charge conservation, the flux of electrons and ions to the electrodes is equal, so the net current (the sum of a positive ion contribution and a negative electron contribution) is zero. Electrons and ions created on one side of the discharge move to the electrode on that side and are lost through recombination.

Although the structure of the discharge shown in Figures 6a,b is much simpler than those found in actual self-sustained discharges, this solution contains a number of features characteristic of more complex discharges. The central region has a small electric field and the electron and ion concentrations are nearly equal in this region. This is due to the fact that a relatively small difference in electron and ion concentration induces a strong electric field that opposes further charge separation. Typical charged particle number densities range from 10^8 to $10^{11}\ \mathrm{cm^{-3}}$. The steady state charged particle number density is, of course, a consequence of the balance between the rate of ionization and the rate of loss of particles to the boundary. If the charged particle number density falls below about $10^6\ \mathrm{cm^{-3}}$, the electric field between the electrodes is not influenced by the distribution of charged particles; that is, the righthand side of Eq. 3 is nearly zero. Near the walls, significant deviations from quasineutrality (i.e., equal number density of electrons and ions) occur. These regions are known as "sheaths," and they are a consequence of the requirement that the flux of electrons and ions to the surface be equal coupled with the differences in electron and ion transport coefficients (mobility and diffusivity). Electric fields form that tend to reduce electron flux and enhance ion flux: electrons diffuse against this field to the boundary and ions are accelerated toward the boundary. Although in actual plasma processing discharges the situation is more complex, this characteristic tendency of ion acceleration in sheaths toward the boundary is responsible for many of the important materials processing characteristics of plasmas.

An important dimensionless ratio that characterizes the role of charged particle number density in determining the electric field profile is the ratio of Debye length to a characteristic discharge dimension. In the example under consideration, the appropriate discharge length scale is L, the electrode separation. The (electron) Debye length is defined (Smirnov, 1981; Ichimaru, 1973) as

$$\lambda_D = (\epsilon_0 k T_e / e^2 n)^{1/2} \qquad (5)$$

The Debye length as defined in Eq. 5 is the characteristic distance over which the potential of a single positive ion is screened



a. Electron and ion density profiles, because of symmetry, only half the discharge is shown
b. Voltage profile for discharge of Figure 5

Figure 6. Basic structure of solution of Eqs. 1–4.

by electrons. A Debye length can be defined for positive ions as well, but the electron Debye length dominates because the electron temperature is usually much higher than the positive ion temperature, for reasons that will be discussed later. When the Debye length is small compared to electrode separation L, then charged particle densities influence the distribution of electric field strength. Another way of stating this is to note that the Debye length is the order of distance over which substantial deviations from quasineutrality can occur, except near electrodes, where the deviation from quasineutrality can be strongly influenced by the magnitude of an applied voltage. In the absence of a large applied voltage at an electrode (compared to the electron random, thermal energy, which is typically a few electron volts), the distance over which deviations from quasineutrality occur is the order of several Debye lengths. Since electron diffusivity is much higher than that for positive ions, an electric field retarding electrons must form to repel electrons and attract positive ions, as discussed above.

It is perhaps worth noting here that there is a similarity between liquid electrolytes and gas plasmas, in that both systems are composed of mobile charged particles. The major structural difference is related to the fact that in the former system, Debye lengths are on the order of molecular dimensions, whereas in weakly ionized gas plasmas, Debye lengths are on the order of hundreds of microns to millimeters. This difference has implications for the structure of the respective systems near boundaries: in electrolytes, deviation from charge neutrality at boundaries is usually treated as a jump discontinuity, while in plasmas, the sheath region attains a finite thickness and plays a key role in both physics and chemistry. Another important difference is that in liquid electrochemical systems, surface chemistry is usually directly related to ion current; that is, the rate of surface reaction is proportional to ion current. In gas plasmas, the role of neutral species created by electron impact dissociation is usually more important than direct ion chemistry at surfaces.

The foregoing discussion has focused on a simplified nonself-sustained discharge, with some external ionizing source maintaining the plasma. Plasmas used in materials processing are usually self-sustained, with either a direct current or radio frequency voltage applied between the electrodes. (Note that the proper way to discuss applied voltages is in terms of *differences* applied to different surfaces). The electric field generated by the applied voltage heats electrons and ions, which through gas phase and sometimes surface ionization (secondary electron emission), create as many charged particles as are lost through recombination. If an electron collides with a neutral molecule with less than the ionization potential of the molecule, ionization will not take place. The ionization cross section is therefore zero below this threshold electron energy. The cross section rises rapidly above threshold, however, so all electrons colliding with the molecule with energies above threshold are capable of ionizing it. Typically, the distribution of electron energies in the discharge is such that only the highest energy electrons are capable of ionization. That is, only electrons in the high-energy tail of the electron energy distribution function can ionize; this results in large changes in ionization for small changes in mean electron energy. The electron energy is determined by a balance between the rate of heating by the applied field and the rate of loss of energy through various inelastic collision processes and other mechanisms. Therefore, in order to predict the rate of ionization, the magnitude of the electric field strength must be known, and an electron energy balance must be solved. In the nonself-sustained discharge discussed above, an electron energy balance was not solved because ionization was provided externally.

For RF discharges in which a time-dependent voltage is applied to the cathode, all quantities will in general be time dependent, so this must be added to the equations as well. The addition of an electron energy balance and solving the time-dependent equations makes the problem more difficult than the case discussed above. In the interest of completeness, it should be pointed out that a possible simplification is to assume that electron energy at any point in space and time is determined solely by the electric field at that point. This is known as the local field approximation, and although it neglects the role of gradients in space and time in determining the local electron energy, the great simplification provided by dropping the electron energy balance makes it worth consideration. Another complication is the possible presence of so-called beam electrons, which are accelerated across the high field sheath region and enter the discharge with large energies. It is thought that these electrons play a dominant role in DC negative glow discharges sustained by the emission of secondary electrons from the cathode. If beam electrodes are important, additional equations describing their number density and energy must be formulated and solved simultaneously.

To date, there have been relatively few RF discharge physics models published. These fall roughly into two categories: self-consistent conservation equation approaches (often referred to as fluid or continuum equations) and kinetic theory approaches (Monte Carlo simulations or the Boltzmann equation). The discussion here will focus on the former approach, which is an extension of the foregoing discussion of the nonself-sustained discharge. The latter approach is discussed in the next section on nonequilibrium effects. Related topics are discussed in a recent review of discharge simulation by Davies (1986), which concentrates on issues surrounding discharge growth (i.e., breakdown).

Apparently the first attempt to simulate in a self-consistent fashion the structure of an RF discharge was the work of Graves and Jensen (1986). In this paper, equations for electron and positive ion continuity, Poisson's equation, and an electron energy balance were solved numerically. The discharge simulated was a parallel plate electrode, capacitively coupled, 13.56 MHz RF discharge. Discharge variables were assumed to vary only with axial position between the electrodes, gas properties were estimates based on typical values for electropositive gases, and a sufficiently high pressure was assumed so that electron and ion motion could be considered to be collisionally dominated. Since all solution variables are functions of time in an RF discharge (driven by a time-periodic voltage at the powered electrode), one is interested in the time-periodic solution. This was found by expanding the unknown solution in a Fourier series in time and solving for the Fourier coefficients at each point in space. Another possible approach is to simply integrate in time to obtain the time-periodic solution. The major contribution of this paper was to demonstrate that numerical solution of conservation equations is possible for RF discharges, and to suggest that this might be a powerful approach for the systematic study of RF discharge physics.

Similar approaches have been taken by a number of other workers, including Richards et al. (1987), Barnes et al. (1987), and Boeuf (1987). RF breakdown was simulated in SF_6 using fluid equations by Thompson et al. (1986). Typical electron and ion density profiles at two times in the 13.56 MHz RF period are shown in Figure 7 from the work of Richards et al. (1987). The ion density profile remains fixed through the period because ions are unable to follow RF fields at such a high frequency. The electron density profile, by contrast, shows considerable modulation at the plasma-sheath boundary; indeed, Figure 7 demonstrates to what extent sheath thickness is modulated through the period.

The work of Boeuf (1987) is noteworthy because of the inclusion of negative ions and comparison to experimental measurements of Gottscho and Gaebe (1986) in which the existence of transient double layers was observed in 50 kHz discharges in BCl_3. The origin of double layers in Boeuf's simulation was reported to be a large modulation in the positive and negative ion density profiles at low to moderate frequency near the plasma-sheath boundary. A typical profile of the electric field in a model electronegative gas from Boeuf's paper is presented in Figure 8. Note the local maxima in electric field magnitude at certain times in the RF period (away from electrode surfaces), which indicates the presence of a double layer. Boeuf (1988) has recently extended this model to two spatial dimensions (DC) with a model electropositive gas.

Although promising, these models of discharge structure are still preliminary and comparisons to experiment, when conducted at all, have been only qualitative. Much more work remains to be done in extending to two spatial dimensions and including all of the important kinetic processes in the discharge. In addition, an exploration of the limitations of the continuum approach needs to be undertaken, boundary conditions can be difficult to specify, and many questions remain about the best way to numerically solve the equations.

Microscopic models and nonequilibrium phenomena

The foregoing discussion involved some implicit assumptions concerning the nature of processes governing discharge structure. In effect, the equations employed imply that the macroscopic properties of charged particles (and their collective behavior) can be described using conventional equations of change: number continuity, momentum and energy balances. Such equations (often referred to as "fluid" equations in the gas discharge literature) can always be defined, but transport and rate coefficients contained within the equations may not be easily evaluated in terms of state variables (for example, particle "temperature"). In effect, our ignorance of the true physics can be hidden in the definition of unknown coefficients. This problem is intimately tied into the fact that the discharge *is not at local thermodynamic equilibrium*. In fact, the discharge is *far* from local thermodynamic equilibrium (LTE); furthermore, this distance from LTE is the major reason that weakly ionized gas plasmas are so useful for materials processing, so the problem cannot be ignored. The conventional equations of change are based on the assumption that local thermodynamic equilibrium exists (strictly speaking, for each species separately), so questions naturally arise about the validity of conventional equations of change when applied to discharge structure. A completely satisfactory treatment of this issue is not only well beyond the scope of the present article, it has never been accomplished in the context of a gas discharge. In this section, a description of nonequilibrium phenomena will be presented along with some suggestions about the proper way to deal with them. There are two major sources of deviation from local thermodynamic equilibrium in the discharge:

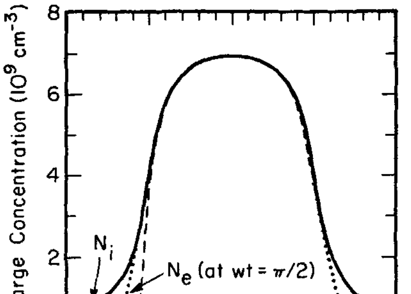


Figure 7. Electron and ion density profiles calculated from a fluid model of RF discharge at 13.56 MHz (Richards et al., 1987).

Two times in RF period are plotted:
For $\omega t = \pi$, electrode at $x = 0$ is near its maximum negative voltage;
For $\omega t = \pi/2$, electrode is near 0 V with respect to opposite electrode

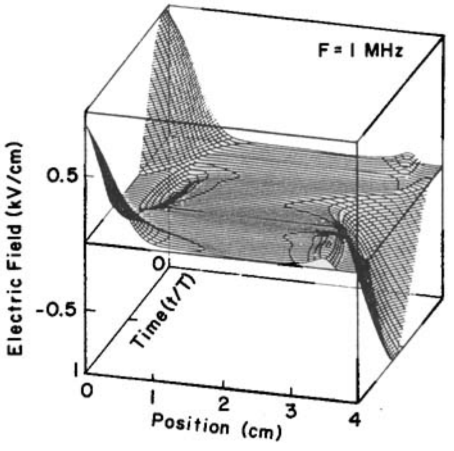


Figure 8. Predicted electric field profile in time and space for a 1 MHz RF discharge in a model electronegative gas (Boeuf, 1987).

1. Electrons throughout the discharge have mean energies that range from 0.1 to 10 eV, while the neutral gas is near room temperature (around 0.03 eV)
2. Ions near boundaries where sheaths form are accelerated to high energies

In the bulk (quasineutral) region, ions are usually near the temperature of the neutrals. (Note that units of electron volts are commonly used in atomic physics and related fields because the ionization potential of most molecules is around 10 eV. The corresponding SI unit is the Joule, with conversion factor 1.602×10^{-19} J/eV. If eV is used to denote the mean energy of a collection of particles with a Maxwell-Boltzmann distribution, then one can use the conversion 11,600 K/eV.)

There are other sources of nonequilibrium, as well. These include excited state *neutral* species such as metastables and vibrationally excited molecules. Metastable molecules (or atoms) are in an excited electronic energy state with long lifetimes. Typical excited electronic states have lifetimes that range from a few nanoseconds to tens of microseconds, but metastables can survive on the order of milliseconds to seconds before being lost. Metastable species can participate in chemical reactions by giving up their excess energy in a "quenching" collision with another molecule or atom, or metastables can collide with electrons, boosting the electron kinetic energy. The latter process is known as a "superelastic" collision because the electron gains rather than loses energy in the collision. Scheller et al. (1988) present evidence that rare gas metastastables participate in discharge kinetics in mixtures of rare and attaching gases. The term "Penning ionization" refers to a collision between a ground state molecule and a metastable that results in ionization of the ground state molecule. The metastable energy level must be at least equal to the ionization potential of the ground state molecule for this to occur. Rare gases (He, Ar, Kr, etc.) are known to form metastable states readily. In discharges with appreciable concentrations of metastable molecules (from 10^8 to 10^{12} cm^{-3}), two-step ionization may be important: electron collisions create metastables in one step, then in a subsequent collision with the long-lived metastable, another electron can ionize the excited state. Since the metastable energy level is below the ionization potential, electrons capable of exciting this transition need have less energy than electrons capable of directly ionizing the ground state molecule. The second step also requires less energy than direct ionization, so it is possible to sustain the discharge through two-step ionization with lower energy electrons than would be necessary for direct ionization (Ferreira and Ricard, 1983).

Vibrationally excited molecules can play an important role in discharge structure, as well. It is generally accepted that rotational and translational energy levels are in local equilibrium (or close to it), due to the rapid rate of energy transfer between rotational and translational energies in neutral molecules. However, vibrational-rotational and vibrational-translational energy exchange rates are appreciably lower, and vibrationally excited molecules are common in low-pressure gas discharges. Recent studies suggest that interaction between electrons and vibrationally excited neutrals can be an important influence on the electron energy balance (Massabieaux et al., 1983; Boeuf and Kunhardt, 1986; Brunet and Rocca-Serra, 1985). Electrons can lose a substantial amount of energy exciting vibrational transitions in some molecules, due to large vibrational excitation cross sections (collision probabilities); as noted above, these molecules typically lose this energy relatively slowly in neutral-neutral collisions. However, superelastic collisions between vibrationally hot molecules and lower energy electrons can transfer some of this energy back into the electron gas, deexciting the vibrationally hot molecule in the process. It is possible that other kinetic processes are accelerated when vibrationally excited molecules are involved, including chemical reactions and surface processes (Capitelli and Molinari, 1980; Capitelli, 1986). Although discharges in atomic gases are emphasized, the monograph of Biberman et al. (1987) provides a good discussion of nonequilibrium kinetic processes in low-temperature plasmas.

The issue of large deviations from local thermodynamic equilibrium centers around electrons. This is mainly because of the primary role electrons play (directly or indirectly) in virtually all important chemical and physical processes in materials processing plasmas. In order to understand the causes of the large deviation from LTE in low-pressure plasmas, several facts concerning electron-neutral collision processes must be in hand. Collisions can be categorized as elastic, inelastic, and superelastic; the probability of each type of collision occurring is a function of the relative velocity between colliding particles (and, of course, of the number densities of colliding particles). An elastic collision involves transfer of only kinetic and not internal energy between collision partners. The maximum fraction of kinetic energy transferred in an elastic collision is the following:

$$\delta = 2m/(m + M) \qquad (6)$$

where m is the mass of the small particle and M is the mass of the large particle. Clearly, when $m \ll M$, the fraction of energy transferred in an elastic collision is small. Since electrons are much less massive than neutral molecules, energetic electrons colliding elastically with neutrals lose relatively little energy.

Inelastic collisions between a high-energy electron and a lower energy molecule involve a loss of electron kinetic energy and excitation of the molecule into a higher quantum energy state: rotational, vibrational, electronic, dissociative, or ionizing transitions are possible. Inelastic collisions are generally characterized by a threshold energy: if particles collide with a relative energy below threshold, then the collision probability (for the inelastic collision) is zero. Above threshold, collision probability is finite. The magnitude of the collision probability is characterized by what is known as a collision cross section (in units of area). Details concerning collision mechanics can be found in most texts on gaseous electronics (von Engel, 1965; Chapman, 1980; McDaniel, 1964; Cherrington, 1979). Threshold for the lowest inelastic collision for molecules (rotational excitation) is typically on the order of a few tenths of an electron volt. Below this energy, electrons experience only elastic collisions. Even a small applied electric field (on the order of 1 V/cm) will supply more energy than the electron can dissipate in elastic collisions at relatively low pressures (Ginzburg and Gurevich, 1960). The result is that electron mean energy rises above neutral gas temperature, until inelastic collisions become important. The highest energy electrons will eventually experience inelastic collisions and mean electron energy will reach a steady state, well above neutral gas temperature. This is the reason that electrons in glow discharges are far from local thermodynamic equilibrium. Ions, on the other hand, have about the same mass as their neutral collision partners, and can lose an appreciable fraction of their kinetic energy in elastic collisions. This tends to keep ion energies close to neutral temperatures, so long as the applied electric field does not become too large. Near the boundary of the plasma, large electric fields form in order to satisfy current continuity. When ions reach these sheath regions, they are accelerated to high energies, resulting in all of the effects on surface processes discussed above.

The distribution of electron energy plays a central role in determining the rates of important inelastic processes such as ionization and molecular dissociation. In addition, electron energy distribution determines electron transport properties. In order to rigorously treat systems far from local thermodynamic equilibrium, recourse must be made to kinetic theory. It has been understood for many years that electrons were not at LTE, and furthermore, that the electron energy distribution does not follow the Maxwell-Boltzmann form (Huxley and Crompton, 1974). It should be realized that it is possible for electrons to not be at LTE but still have a Maxwellian energy distribution; that is, the concept of an electron temperature different from the neutral gas temperature can be valid. The only practical way for this to occur, however, is for electron-electron collisions to dominate electron-neutral collisions such that electrons "Maxwellianize" among themselves. This process occurs through long-range Coulomb interactions, but is effective only when electron density is sufficiently high. For typical discharge conditions, the minimum electron density for electron-electron collisions to be important is about 10^{12} cm^{-3}. This density is about an order of magnitude higher than is normally found in glow discharges, so electron-electron collisions are usually negligible under conditions of interest. Therefore, we conclude that the assumption of an electron temperature under conditions of interest is seldom valid. It may be, however, that the assumption is not so inaccurate as to be useless.

There is a large literature on electron collisions and transport in gases, including experimental measurements using electron beams (Brown, 1979) and electron swarms (Huxley and Crompton, 1974; Lindinger et al., 1984). Scattering from crossed beams of electrons and neutrals is typically used to determine collision cross sections directly for electron energies above about 1 eV (experimental difficulties arise with lower energy electron beams); swarms are used to directly measure rate and transport coefficients and are useful in estimating collision cross sections for electron energies below 1 eV. The major theoretical problem in swarm analysis is to relate rate and transport coefficients observed in swarm experiments to collision cross sections. The solution procedure involves iterating on trial collision cross sections until predicted rate and transport coefficients match measured values. Predictions are based on either a numerical solution of the Boltzmann equation or particle simulations (a Monte Carlo method) in order to find the electron energy distribution function, from which rate and transport coefficients are calculated. It is beyond the scope of this article to discuss this procedure in any detail, and the interested reader is referred to the original literature (Huxley and Crompton, 1974, and references therein; also, Penetrante and Bardsley, 1984; Pitchford et al., 1981; Reid and Hunter 1979). Additional references that provide a good perspective on related issues are: Shkarofsky et al. (1966), Allis (1956); and Ginzburg and Gurevich (1960). Application of these approaches to studies of gas discharge lasers is discussed by Cherrington (1979).

The question naturally arises: why not solve the Boltzmann equation (or equivalently, apply the Monte Carlo method) to simulate conditions in gas discharges? The answer is that this can be done (relatively easily) using established techniques as long as the electric field does not vary significantly in space, or if the field profile is specified (Kushner, 1983; Boeuf and Marode, 1982; Winkler et al., 1987; Moratz et al., 1987; and Sato and Tagashira, 1985). Some work has been done in solving the Boltzmann equation for electrons assuming only forward and backward scattering, along with the ion continuity equation and Poisson's equation for a DC glow discharge (Long, 1979; Duke, 1985). However, it is difficult to see how this approach could be readily extended to the discharges typically used in plasma processing.

There is undoubtedly a great deal of work that remains to be done in understanding the macroscopic implications of microscopic nonequilibrium phenomena for processing discharges. However, it appears that much can be learned from a purely macroscopic approach, using the fluid equations or macroscopic equations of change, coupled with Poisson's equation. The complexity of conditions in chemically reacting, weakly ionized gas discharges suggests that a variety of simulation approaches will be developed to suit a variety of purposes. Macroscopic equations of change are relatively easy to solve, but have limitations that may be important. Kinetic theory approaches are possible, but need much further development to be applied to processing discharges, and will probably be relatively expensive computationally since they provide information about the distribution of particle energy. A potentially promising approach is to combine fluid equations and particle simulations into a hybrid code, exploiting the advantages of each: the fluid equations can be made self-consistent and a particle simulation can account for nonequilibrium effects. This has yet to be attempted for weakly ionized gas discharges, to the author's knowledge.

Discharge stability

The topic of discharge stability is important for gas discharge chemical reactors because it is not uncommon for stability limits to determine the range of conditions under which a reactor can operate. For example, it is necessary for the discharge to be "ignited" and in the appropriate mode of operation in order for desired chemical and materials processing effects to be achieved. The importance of this topic notwithstanding, there has been little discussion of stability in the plasma processing literature. It has been noted that addition of noble gases (Ar or He, typically) will stabilize plasmas of electronegative gases that tend to constrict or oscillate (Flamm and Donnelly, 1981). Sawin et al. (1985) observed instabilities and hysteresis in chlorine discharges used for etching polysilicon films. These authors suggested that this was a manifestation of multiple steady states. An intriguing example of unstable plasma reactor behavior is the case of reactive sputtering of metal targets. Affinito and Parsons (1984) point out that abrupt transitions in reactive gas pressure (e.g., nitrogen or oxygen) are known to occur when discharge current or power is varied over certain ranges and the flow rate of the reactive gas is held constant. A similar transition occurs when reactive gas flow is varied and power or current is kept constant. The abrupt transitions are accompanied by hysteresis, which not only suggests that multiple steady state behavior is involved, but that it can restrict the accessible range of operating conditions. Workers have commonly attributed reactive sputtering instabilities to surface phenomena such as gettering and formation of target surfaces with different electrical properties (Affinito and Parsons, 1984; Maniv and Westwood, 1980; Shinoki and Itoh, 1975), leading to positive feedback and subsequent transition between different operating conditions. There seems to be some similarity between these proposed mechanisms and those of passive film formation on the stability of electrochemical systems (Talbot, 1986).

The general problem of finding stable conditions under which to operate a reactor is currently treated by searching for the combination of pressure, power, frequency, reactor geometry, and reactant gas composition that yields a stable discharge. One of the purposes of this section is to suggest that techniques commonly used in chemical engineering to analyze reactor stability can be applied to problems of discharge stability.

There is a history of research into the phenomena and causes of glow discharge instabilities; some of this history is presented in the review by Allis (1976). The direct current discharge positive column has received the most attention because gas discharge lasers and fluorescent lighting tubes commonly employ the positive column. Instabilities most often observed in the positive column of DC discharges are:

1. An abrupt constriction as pressure and/or current is raised above some critical value
2. Traveling or stationary luminosity waves known as striations

These instabilities are not yet fully understood even in DC discharges, and implications for RF discharges used in materials processing applications are far from clear. It is observed that discharges in gases with large electron affinities (electronegative gases such as the halogens) tend to be more unstable than discharges in electropositive gases (Emeleus and Woolsey, 1970). However, there is evidence that constriction (and a related phenomenon, the glow-to-arc transition) is associated with a thermal instability (Allis, 1976; Jaeger et al., 1976; Nighan and Wiegand, 1974a, b; Wasserstrom and Crispin, 1982; Bondarenko et al., 1979; Ecker et al., 1964; Eletskii and Smirnov, 1971). The thermal instability involves a positive feedback between an increase in current and gas heating. As the gas is heated by the passage of current, gas density decreases (at constant pressure). Since the rate of ionization depends on the ratio of electric field to gas density (E/n), a decrease in gas density is equivalent to an increase in electric field and causes a corresponding increase in ionization rate. The increase in ionization rate increases electron density, which results in a still higher current in positive feedback. If the rate of heating becomes sufficiently high, thermal ionization will occur (that is, ionization due to collisions between neutral species), leading to arc formation.

A common approach to discharge stability is through voltage-current plots. Characterization of stability with electrical arguments has been pursued in the electrochemical literature as well. Wojtowicz (1972) and Talbot (1986) present discussions of mathematical models of electrochemical oscillations, including those based on electrical considerations. This approach reflects the fact that the discharge (or electrochemical cell) is one part of an electric circuit that includes a voltage (or current) source and some other impedance. Circuit stability can be related to the shape of the voltage-current characteristic.

The circuit operating points are found by plotting the discharge voltage-current characteristic along with the "load line," which represents the voltage-current characteristic of the rest of the circuit. It is obvious from Figure 9 (Cobine, 1941) that multiple current values can exist for a given battery voltage V_1, if the external circuit has resistance R_2. The low-current part of the characteristic, with a rapidly rising voltage for a small change in current (with intersection at point A), is termed a "dark" discharge. The currents in this regime are typically on the order of microamperes. The transition to a glow discharge occurs beyond point S, where dI/dV for the discharge cell becomes large, and the current is typically around 10^{-5} amp. Point S on the curve corresponds to the sparking voltage V_S (Cobine, 1941), which is the transition that may be termed breakdown or ignition to a "normal" glow discharge (from point S to point B). After point B, the voltage begins to rise for a change in current, and this has been termed the "abnormal glow" discharge. A second abrupt transition is possible, as the voltage-current characteristic declines again. This last transition is known as the glow-to-arc transition: current increases by orders of magnitude and voltage drops. The discharge becomes more fully ionized, and typically, thermal phenomena play an important role. The region beyond point D corresponds to an arc discharge. Arcs are commonly used, for example, in welding and other high-temperature processes. These discharges are not used in microelectronics materials processing and will not be discussed further except to note that the glow-to-arc transition may represent an upper limit in current and/or pressure for glow discharges. This kind of instability does not involve a transition into a full arc in typical processing discharges, but rather filamentary sparks will appear, accompanied perhaps by intermittent pulsing.

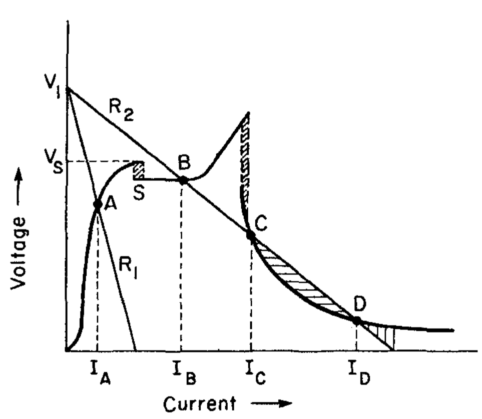


Figure 9. Voltage-current characteristic (dark line) and load lines (for two external circuit resistances R_1 and R_2) for a typical DC glow discharge (after Cobine, 1941).

Intersections are possible discharge operating points; multiple steady states exist for certain values of external circuit resistance, suggesting an analogy with chemical reactor stability

Stability of the operating points in Figure 9 depends on the relative slopes of intersecting lines. For example, points B and D are stable, but point C is unstable. This is expressed in the following terms,

$$dV/dI + R > 0 \tag{7}$$

where dV/dI is the slope of the voltage-current characteristic and R is the external circuit resistance. Sometimes dV/dI is termed a differential resistance, and "negative differential resistance" is associated with unstable electrical characteristics in a variety of fields from electrochemistry (Talbot, 1986) to semiconductor devices (Sze, 1981; Ridley, 1963). In fact, there is an entire class of solid state electronic devices used as microwave oscillators known as negative differential resistance oscillators. The current-voltage characteristic of a metal insulator semiconductor (MIS) switch diode is shown in Figure 10 (Sze, 1981). There is a high-impedance, low-current "off" state and a high-current, low-impedance "on" state. The transition from "off" to "on" occurs at the switching voltage. Other devices displaying similar behavior include the Shockley diode and thyristors. Chemical engineers will see the analogy to reactor multiple steady states.

There have been suggestions that analogous behavior in gas discharges could be exploited to produce radio frequency oscillation devices (Lopantseva et al., 1979). As discussed by Ridley

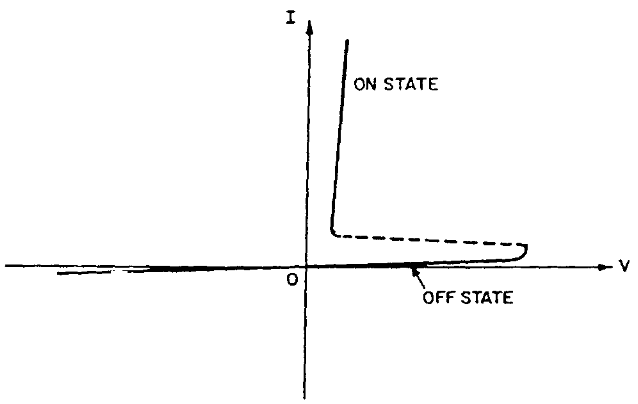


Figure 10. Voltage-current characteristic for an MIS switch diode (Sze, 1981).

---- Unstable region between off (high-voltage, high-impedance) state and on (low-voltage, low-impedance) state

(1963), it is possible to have voltage-controlled (multiple voltages for a given current) or current-controlled (multiple currents for a given voltage) negative differential resistance. The latter case is associated with gas discharge breakdown and the glow-to-arc transition, involving the formation of high-current filaments running along the field direction. The former case is associated with formation of traveling domains in which moving regions of high electric field separate regions of low electric fields. The interfaces that separate high and low field domains are perpendicular to the direction of the current, and appear to bear some resemblance to gas discharge striations. It is tempting to conclude that the current-controlled case corresponds to constriction and the voltage-controlled case corresponds to striations, thereby associating the most commonly observed glow discharge instabilities with corresponding instabilities in semiconductors. However, because of the lack of firm evidence, this association is at present only speculative. Note that there is a similarity between electron and hole transport, creation and loss in semiconductor devices, and the corresponding features of electrons and positive ions in gas discharges. Sabadil (1968) has proposed an analogy between the well-known Gunn instability in semiconductor devices (Sze, 1981) and instabilities observed in oxygen discharges.

There have been a number of attempts to understand glow discharge instabilities by direct simulation of discharge structure. Grabec (1974), for example, solved a reduced set of macroscopic equations of change for the positive column of a DC discharge. Quantitative agreement between predicted striation structure and experimental measurements was achieved in this work. Among the conclusions was that the exponential dependence of ionization rate on electron mean energy (or temperature, when the assumption of an electron Maxwell-Boltzmann distribution function is made) is the key to the observed relaxation oscillations. The function used for ionization rate dependence on electron temperature is similar to the Arrhenius form for a chemical reaction rate coefficient:

$$k_{ionization} = A(T_e)\exp(-eV_i/kT_e) \tag{8}$$

where $A(T_e)$ is a relatively weak function of electron temperature, V_i is the ionization potential, and k is Boltzmann's constant. It is of course the existence of such strongly nonlinear terms in conventional chemical reactor models that results in multiple steady states and a variety of instabilities, including oscillations, traveling waves, abrupt transitions, and other phenomena (Schmitz, 1975). There has been some discussion in the literature (especially the Soviet literature) of the relationship between discharge stability and multiple steady states, hysteresis, oscillations, and so on (Barkalov and Gladush, 1979; Tsendin, 1985; Golubovskii and Sonnenburg, 1979a, b; Nedospasov, 1968; Knorr, 1984).

The presence of large concentrations of negative ions in a discharge has been associated with a variety of instabilities. Both constriction and striations occur more readily in discharges in electronegative gases such as the halogens (Emeleus and Woolsey, 1970). Oscillations have been reported in discharges of electronegative gases by a number of workers (Barkalov and Gladush, 1979; Kovalev et al., 1982a, b; Morrow, 1985; Chaudri et al., 1980, 1984). One source of the oscillations seems to be nonlinearities involved with electron attachment and detachment kinetics, coupled with normal ionization kinetics.

A considerable effort has been made to understand instabilities associated with molecular gas lasers, and in particular the role of negative ion processes on laser stability. Haas (1973) treated a homogeneous discharge (i.e., no spatial variations) and examined linearized stability equations to determine the cause of the onset of unstable operation in time and space. For a locally uniform plasma, fluctuations within the plasma were found to excite several wave modes, including ionization, negative ion production, and (neutral species) vibrational relaxation modes. The relative importance of each of these possible routes to instability was found to depend upon:

1. The relative electron and gas temperature dependences of the charged particle production and loss processes (especially ionization, attachment and detachment)
2. Electron temperature dependence of electron energy losses to vibrational and electronic excitation
3. Gas temperature dependence of the rate coefficient for vibrational-translational relaxation and the gas thermal conductivity for vibrational energy transfer
4. Steady state plasma properties such as gas mixture, degree of ionization, electron temperature, negative ion density, and the ratio of electron to neutral gas vibrational temperature.

Not all of these properties in 4 above are independent of one another.

This very comprehensive study was followed by a paper by Nighan and Wiegand (1974a), in which the importance of the relative electron temperature dependence of the electron-molecule attachment rate coefficient compared to the ionization rate coefficient is emphasized in the onset of typical discharge instabilities in molecular gas lasers. The instability that can occur is illustrated in Figure 11. An initial disturbance increasing electron density typically results in a decrease in local electron temperature due to space charge effects, but the net effect of this on discharge stability depends on the nature of the electron creation and loss kinetics. The upper path in Figure 11 is for recombination dominated plasmas, in which a decrease in electron temperature results in a decrease in electron density. This leads to negative feedback and stability. If, however, electron attachment (to form negative ions) and detachment (from negative ions to create free electrons) kinetics are important, then it is possible that positive feedback can result. The instability can occur if the electron temperature dependence of the ionization

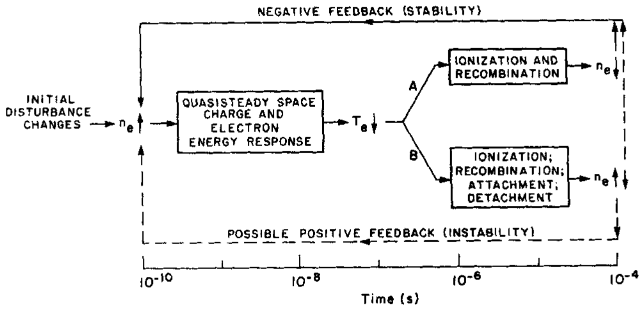


Figure 11. Proposed mechanism for discharge instability caused by nonlinear electron creation (ionization, detachment) and loss (attachment) kinetics in electronegative gas discharges (Nighan and Wiegand, 1974).

rate coefficient is less than the attachment rate coefficient dependence: when electron temperature decreases, the ionization rate decreases less than the attachment rate, and the net effect is an *increase* in electron density. Since the original perturbation was an increase in electron density, a positive feedback results. This has been termed the ionization-attachment instability.

There is evidence that discharge kinetic instabilities are not restricted to DC discharges. Levitskii (1958) was the first to point out that high-frequency RF discharges could exist in one of two qualitatively different modes: the α discharge and the γ discharge. The terms follow from the dominant mode of ionization: the α discharge is sustained through volume ionization and the γ discharge is sustained through secondary electrons released from electrode surfaces. [The terms originated in the early gas discharge literature in which Townsend named the "first," α, and "second," γ, ionization coefficients to correspond to volume and surface ionization, respectively (von Engel, 1965).] The transition from one discharge form to the other was reported to be abrupt and accompanied by hysteresis. This idea was more fully articulated and experimental evidence in support of the mechanism proposed by Levitskii (1958) was presented by Yatsenko (1981). More recently, Godyak and Khanneh (1986) presented new experimental data and a model of the transition. This work, which was apparently largely unknown in the Western literature until quite recently, indicates the more advanced state of the Soviet gas discharge physics literature. For a further discussion of differences in development of the Soviet and Western literature on gas discharge physics, the interested reader may refer to the monograph of Godyak (1986).

Discharge Chemistry: Diagnostics and Modeling

Introduction

The area of discharge chemical diagnostics has seen considerable progress lately, in particular with the application of laser spectroscopy to detection of reactive intermediate species that are thought to play a decisive role in materials processing. When laser spectroscopy can be applied, there are usually few techniques that are more powerful. The major drawbacks to the variety of laser spectroscopies are that they cannot always be applied to species of interest, the experimental setups are often expensive, and some techniques require substantial experience. Besides laser spectroscopy, other common diagnostic techniques include optical emission spectroscopy (OES) and mass spectroscopy (MS). These tools have been the traditional mainstays of plasma diagnostics, although each has its limitations: OES is usually difficult to interpret, and MS often suffers from uncertainty associated with sampling bias and complex cracking patterns.

There is a need for reliable, systematic models of discharge chemistry. In particular, measuring only a few species profiles in a discharge is inadequate if a detailed mechanistic understanding of discharge chemistry is to be obtained. From studies of flame and atmospheric chemistry, it is known that dozens of species can participate in discharge chemistry through hundreds of elementary reactions. In order to systematically deal with this complexity, mathematical models of sources, sinks, and transport of chemical species must be used. This will require that fundamental studies of individual elementary reaction rates be made, probably in isolated systems, free from competing reactions. Well-characterized test systems must be developed for plasma chemistry studies; an example from the field of combustion is the premixed flat flame burner. Work has begun along these lines, and will be discussed in this section. It is clear that much remains to be done, but with guidance from other areas in which similar problems have been attacked with success, the prognosis appears bright.

It is obvious that surface chemistry plays a key role in materials processing technologies that aim to modify surfaces, either through deposition or removal of a film. Unfortunately, little progress has been made in understanding surface chemistry in plasmas. The reasons for this include the common difficulty with surface chemical analysis: the best diagnostics can only be applied in ultrahigh vacuum (UHV), and practical plasma systems involve poorly characterized surface layers in the presence of various types of energetic particle bombardment. Strategies used to overcome these difficulties include completely *ex situ* studies in which model systems are treated in UHV, and studies in which a surface is transferred under vacuum from a plasma environment to UHV for analysis. Once again, we can learn from other fields in which similar problems are encountered, such as heterogeneous catalysis, heterogeneous combustion, and thermal chemical vapor deposition. In these fields, although progress has been made (particularly in catalysis), many questions about fundamental surface processes remain; understanding of gas phase processes is much more advanced. We should therefore not expect progress in understanding plasma surface chemistry to proceed as rapidly as studies of gas phase chemistry.

Optical gas phase diagnostics

Optical techniques are popular diagnostics because one can usually avoid problems associated with extraction probes, the most important of which is sample bias due to interaction of the probe with the sampled environment. There are several excellent reviews available focusing on optical diagnostics in materials processing plasmas (Gottscho and Miller, 1984; Dreyfus et al., 1985; Wormhoudt et al., 1983). The present treatment will therefore be an introduction and overview of the most important developments and applications to date.

The most widely applied optical diagnostic is optical emission spectroscopy (OES), in which photons (from infrared to ultraviolet wavelengths) emitted naturally by the plasma are collected and spectrally resolved with a monochromator and photomultiplier tube. This technique is therefore completely nonintrusive, and offers information about plasma structure, composition, and properties. Plasma emission arises from a variety of sources, but generally involves the transition of a molecule (or atom or ion) from an excited electronic state to the ground electronic state (or an intermediate state), emitting a photon in the process. The key to interpreting the emission is in identifying the route to excitation. The two most common excitation routes are:

1. Direct electron-impact excitation of ground state species
2. Dissociative excitation, resulting in an excited molecular fragment.

Each of these processes can be represented schematically by treating excitation and deexcitation as chemical reactions. Direct electron impact excitation followed by radiative decay is represented as follows:

$$A + e^- \rightarrow A^* + e^- \tag{9}$$

$$A^* \rightarrow A + h\nu \tag{10}$$

where A represents the ground electronic state, e^- represents the energetic electron responsible for excitation, A^* represents an excited state, and $h\nu$ represents the emitted photon. After excitation, the excited state decays back to the ground state (or, more generally, some lower energy state) with concomitant photon emission. Note that a complication not always recognized in OES is the existence of cascading energy states: a higher energy level decays to ground level, but only after intermediate "stops" at intermediate energy levels, emitting a photon at each transition. Such cascades are generally ignored, but they may play an important role in emission. Radiative lifetimes are usually characterized by a single time constant (exponential decay) on the order of 10^{-8} s. The upper state can also decay through collisions, but at pressures on the order of 1 torr (133 Pa) and below, collisions can usually be neglected as an excited state loss process, as long as the radiative decay is sufficiently rapid. The second major type of emission results from dissociative excitation:

$$AB + e^- \rightarrow A^* + B + e^- \tag{11a}$$

$$A^* \rightarrow A + h\nu \tag{11b}$$

where the molecule AB is dissociated by electron impact and A is created in an excited state. Subsequent decay to the ground state results in emission.

Major interest in emission spectroscopy has centered on the possibility of measuring the concentration of (ground state) reactive intermediates, some of which are known to play a role in etching and deposition. The rate of excitation can be expressed as follows:

$$R_{excitation} = k_{ext} n_e n_x \tag{12}$$

Since most excited states are short lived (tens of nanoseconds to microseconds, typically), it is often assumed that the rate of emission is identical to the rate of excitation. The excitation rate coefficient is a function of the electron energy distribution function and the collision cross section for excitation in the following way:

$$k_{ext} = \int_0^\infty (2/m_e)^{1/2} \epsilon^{1/2} \sigma(\epsilon) f(\epsilon)\, d\epsilon \tag{13}$$

Typically, one is interested in determining n_x from emission intensity changes corresponding to changes in, for example, pressure, power, or gas composition. The problem is that both n_e and k_{ext} are, in general, functions of these parameters as well as n_x. In order to "cancel" the dependence of electron density and rate coefficient changes, a technique known as emission actinometry is used (Coburn and Chen, 1980; d'Agostino et al., 1981, 1983, 1984).

Another important application of optical emission spectroscopy is to obtain information about electron dynamics. In some cases, emission profiles can be used to infer the behavior of electrons in time and space. For example deRosney et al. (1983), Bletzinger and DeJoseph (1986), and Barnes and Winslow (1978) examined 13.56 MHz RF discharges in silane, nitrogen, and oxygen, respectively. Each of these workers observed time- and space-dependent emission patterns that peak around the cathodic (momentary negative) electrode and move toward the center of the discharge during the RF period. By contrast, Flamm and Donnelly (1986) report that the emission in chlorine discharges peaks near the *anodic* phase of the cycle. It may be that the difference is due to the fact that chlorine is strongly electron attaching, while the other gases are not.

Graves (1987) suggested that emission pattern (in the nonattaching gases) is due to the characteristic nature of electron motion in the plasma-sheath region, based on results from fluid model simulations. It has also been suggested (P. Bletzinger, personal communication, 1987) that these luminous waves can be explained as electron acoustic waves (i.e., electron pressure gradient driven). Jurenka and Barreto (1982), also using a fluid analysis, estimated from analysis of the electron momentum balance equation that the wave velocity should be on the order of 10^6 m/s. This is close to the velocity measured by deRosney et al. (1983): 1.7×10^6 m/s.

Laser-induced fluorescence

The major disadvantage of OES is related to the fact that emission is directly related to *excited* state concentration, but we usually are more interested in the ground state population. Furthermore, the relation between the excited state and ground state can be difficult to establish quantitatively. A technique that overcomes this limitation is laser-induced fluorescence (LIF). LIF (Dreyfus et al., 1985; Karlicek et al., 1983; Gottscho and Miller, 1984; Crosley, 1980) involves laser-generated photons exciting species from ground electronic states to excited electronic states, followed by collection of fluorescence photons as the excited state decays to a lower energy state. A typical LIF setup is shown schematically in Figure 12. A pump laser (usually either a pulsed excimer, nitrogen or Nd:YAG laser) excites (pumps) a tunable dye laser. The laser output is directed and perhaps focused to a specific location in the plasma, at which excitation occurs. The resulting fluorescence signal is collected (at 90 degrees from the laser pulse) by a lens focused on the excitation spot, and the fluorescence is imaged onto the inlet slit of a monochromator (or may be sent through a filter). The spectrally resolved (or filtered) light is recorded by the photomultiplier tube (converted into an electronic current), the signal

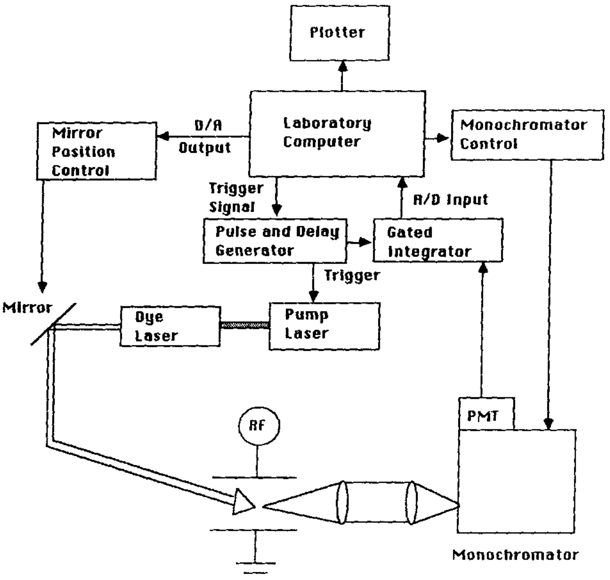


Figure 12. Typical (pulsed) laser-induced fluorescence experiment.

Pulse generator triggers pump laser, which excites the tunable dye laser; computer control of experiment is essential

is amplified and usually sent into a boxcar integrator. The latter device utilizes so-called gated detection, in which the signal is looked for only during a very narrow gate in time (ranging from several nanoseconds to hundreds of microseconds, depending on the application). This method results in excellent sensitivity because the gate is chosen to coincide with the timing of the laser pulse (after accounting for delays in the electronics). This helps to discriminate the LIF signal from background plasma emission, which is often the factor determining minimum signal detection level. The entire process is repeated at rates typically ranging from 10 to 100 Hz. The entire experiment is best controlled by a computer in order to automate the firing of the laser, the timing of data collection, scanning of the monochromator, movement of the optics, and so on.

LIF can be more quantitative than OES because the experimenter controls both wavelength (energy) and number of exciting agents (photons). In effect, photons with known characteristics replace electrons with unknown density and energy distribution as the excitation agent. In addition, the photons are nearly monoenergetic and they can be directed to a specific position in the discharge at a specific time. The spectral, spatial, and temporal resolution of LIF is therefore excellent. Obtaining ***absolute*** concentrations requires that the collection efficiency of the optics be known, the volume of excitation must be known, and a number of spectroscopic constants must also be available (Donnelly et al., 1982). Alternatively, the LIF signal can be calibrated with another technique which provides absolute concentrations more easily (such as absorption). Even if this information is not available, however, LIF can provide relative concentration profiles.

In addition to concentration measurements, LIF can access individual quantum states (rotational and vibrational), and therefore measure rotational and vibrational "temperatures." In fact, one can test whether the distribution of energies corresponds to a Boltzmann distribution and therefore qualifies for the term temperature. Generally, it is found that rotational states are equilibrated with translational energy levels in discharges, but vibrational levels are different and elevated compared to translational levels. Davis and Gottscho (1983) describe such an application in CCl_4, mixtures of CCl_4 and N_2, and pure N_2 discharges. It was found that estimates of rotational temperature from optical emission and LIF agreed satisfactorily.

A particularly noteworthy application of LIF is the work of Gottscho and coworkers in developing the technique of Stark-mixed LIF for determination of electric field strengths (Moore et al., 1984; Mandich et al., 1985; Gottscho and Gaebe, 1986). In this work, LIF from the BCl radical (created by molecular dissociation from BCl_3) is used to measure the local electric field with excellent temporal and spatial resolution. The minimum field measurable by Gottscho and Gaebe (1986) using BCl as the probe molecule and a pulsed dye laser (pumped by a nitrogen laser) was about 75 V/cm, which restricts measurement to the high-field sheath regions. However, using NaK as the probe molecule and a cw (continuous wave) ring dye laser, Derouard and Sadeghi (1986) have been able to measure much smaller fields (<20 V/cm). The importance of electric field strengths in discharge processes coupled with the difficulty of measuring them makes this a particularly important development.

Resolution and sensitivity are the strengths of LIF measurements of species concentrations. The minimum detection limits for LIF vary with the species measured. Typical numbers range from 10^6 to 10^9 cm^{-3} (Wormhoudt et al., 1983), seven to ten orders of magnitude below bulk gas density at room temperature and 1 torr (3.54×10^{16} cm^{-3}). The three major limitations to LIF are (Dreyfus et al., 1985):

1. The species to be detected must fluoresce with a reasonable quantum efficiency
2. Background and scattered laser light must be kept to a minimum to avoid overwhelming the fluorescence
3. The tunable laser source must be capable of matching an appropriate transition for the species of interest

The first limitation has to do with the fact that in order for the excited species to be detected, it must fluoresce after being excited. For polyatomic species, the excited state can decay through transfer of excess energy to internal vibrational and rotational transitions. Another problem is that the species may photodissociate before fluorescing. At higher pressures, collisional quenching (transfer of excitation energy to another species in a collision) can be a major problem. This is usually not a major problem at pressures in common use for plasma processing (the issue revolves around the ratio of the rate of radiative decay to the rate of collisional deactivation of the excited state), but it has been an important consideration in higher pressure applications such as combustion (Crosley, 1981; Schofield and Steinberg, 1981). However, in order to relate LIF intensities to level population densities as conditions such as pressure, temperature, and composition change, the analyst must be concerned about quenching rates, collisional redistribution of rotational states, monochromator bandpass, and similar issues. A good discussion of these problems and their resolution is given by Gottscho et al. (1982) for discharges in CCl_4, monitoring LIF from CCl radical. The second limitation (background and scattered light contamination) can usually be handled using gated detection, although LIF detection of SiH_2 has not been possible in discharges (so far) due to scattering from particulates (Dreyfus et al., 1986).

The third limitation (accessibility of the lowest electronic excited state) is a serious one, particularly for detection of important atomic species such as F, O, H, Cl, and others. The lowest energy electronic transitions for these atomic species are in the vacuum ultraviolet, beyond the reach of commercially available tunable lasers (currently, the lower limit of commercial systems using frequency doubling crystals is about 200 nm). There are a number of ways to overcome this difficulty, including the use of two-photon excitation (Gottscho and Miller, 1984; DiMauro et al., 1984; Dreyfus et al., 1985), in which excitation is achieved through the nonlinear interaction of two photons to boost the species to the desired excited state. This requires powerful pump lasers (the rate is second order in photon density) and can involve complications in actual discharge environments because transitions other than the desired one can occur in the presence of large photon fluxes (e.g., multiphoton ionization, photodetachment, photodissociation, etc.). It should also be mentioned that the cost of a typical LIF system, including optical accessories (lenses, mirrors, etc.), signal collection electronics, and lasers, is considerable. Current prices and commercial manufacturers can be obtained from industry directories (e.g., *Lasers and Applications,* IV[13], 1986).

Even though limitations to LIF exist, it is clearly a powerful tool that has only begun to be applied to plasma processing systems. An estimate of the role that can be played by LIF and other laser diagnostics can be made by noting progress achieved in related fields. These include combustion (Crosley, 1980; Lucht, 1987; Smyth and Miller, 1987), plasma fusion (Benenson and Kwok, 1982), and chemical vapor deposition (Breiland et al., 1986a, b; Donnelly and Karlicek, 1982; Karlicek et al., 1983). In each of these areas, LIF and other laser diagnostics have provided information on chemical and physical processes crucial to the development of mathematical models. There is little doubt that in systems characterized by complex chemistry in difficult-to-probe environments that laser spectroscopic techniques will continue to play an important role.

Other laser spectroscopies

There are several other laser spectroscopies that complement LIF and will probably become more important in applications in the future. These include tunable diode (infrared) laser absorption (Wormhoudt et al., 1983, 1987), laser optogalvanic spectroscopy (Taillet, 1969; Walkup et al., 1983; Gottscho and Gaebe, 1986; Kramer, 1986; Goldsmith and Lawler, 1981; Webster and Rettner, 1983), and laser Raman spectroscopy (Hargis, 1981; Lapp, 1980; Eckbreth, 1980). The major disadvantages of absorption methods are that sensitivity is reduced compared to resonance fluorescence and absorption is a line of sight technique, requiring inversion methods to reconstruct spatial profiles. The major advantage of absorption is that it can often be applied when fluorescence cannot. Laser absorption spectroscopy has been used successfully for fundamental studies of rate coefficients when absorption pathlengths can be made conveniently long. The absolute rate constant for SiH_2 (silylene) reacting with molecular deuterium was made by Jasinski (1986) using excimer laser photolysis of phenylsilane, followed by SiH_2 absorption with a ring dye laser. A similar measurement using LIF was made by Inoue and Suzuki (1985). Silylene is thought to be a key intermediate in both CVD (Chemical vapor deposition) and plasma processing for amorphous silicon film deposition from silane, and previous estimates of its loss rate kinetics were shown to be in error by four orders of magnitude (Jasinski, 1986). Jasinski et al. (1984) were able to measure SiH_2 profiles in DC discharges of silane and disilane using frequency modulation absorption spectroscopy. The work of Jasinski et al. (1984) is evidently the first and only time SiH_2 has been detected in a discharge, since attempts to detect SiH_2 with LIF in a discharge have apparently been unsuccessful.

Laser optogalvanic spectroscopy involves the action of the laser pulse changing the charged particle balance in the discharge, thereby altering voltage or current. This can be a sensitive technique because of the possibility of charge amplification in the discharge. This technique is promising from the point of view of understanding discharge structure because mechanisms responsible for maintaining the discharge are involved in generating an optogalvanic signal. The major disadvantage of laser optogalvanic spectroscopy is the difficulty in interpreting the signal due to the complexity of discharge kinetics. However, this feature makes optogalvanic spectroscopy ideal for testing discharge models. This technique has been used in flames (Berthoud et al., 1983); in studies of the effects of metastable population on rare gas discharges (Smyth et al., 1978); as a Rydberg state (Stark effect) spectroscopy to infer electric field strengths in DC discharges (Ganguly and Garscadden, 1985; Doughty and Lawler, 1984); to detect negative ions via photodetachment in RF discharges (Taillet, 1969; Kramer, 1986; Gottscho and Gaebe, 1986); to measure reactive intermediates (Smyth and Taylor, 1985); and to measure ion motion through the cathode fall of a DC discharge (Walkup et al., 1983). The versatility of this technique makes it quite attractive and it should continue to receive attention as a discharge diagnostic.

Laser Raman spectroscopy techniques have received relatively little attention in plasma processing studies. Spontaneous Raman spectroscopy (Hargis, 1981; Lapp, 1980), although widely applicable, suffers from low sensitivity; LIF is orders of magnitude more sensitive. Interference from scattered laser light and unwanted fluorescence can mask spontaneous Raman signals. Coherent Raman spectroscopy (e.g., coherent anti-Stokes Raman spectroscopy or CARS; Eckbreth, 1980) is more sensitive, but is more difficult to apply. Hargis (1981) has pointed out that spontaneous Raman sensitivity can be improved by using pulsed UV lasers, assuming that some method to filter the laser fundamental can be found. A butyl acetate liquid filter was found to very efficiently reject 248 nm scattered laser light from a KrF excimer laser. Raman techniques seem best suited to temperature and major species concentration profiles. An example of spontaneous Raman spectroscopy in CVD studies is the work of Breiland et al. (1986a). In this work, Raman scattering was used to determine both gas phase temperature (from about 200 to 700°C) and silane density profiles (with a resolution on the order of $0.1 \times 10^{16}\ cm^{-3}$).

Mass spectroscopy

Of the nonoptical methods in use in plasma processing, mass spectroscopy (MS) has received perhaps the most attention as a method to detect neutral and ionic species. The major problem with MS is sampling: it is necessary to transport species to be detected from the discharge into the mass spectrometer, involving either a molecular beam technique (sampling through a pinhole in a wall) or an extractive probe. The question of how sampling affects signal intensities can be difficult to answer unambiguously. Interpretation of cracking patterns is also a problem in chemically active plasmas. One problem with direct sampling is that reactions can occur before sampled species reach the ionizer and mass filter, distorting measured profiles. Also, the presence of an extractive probe involves probe disturbance of the plasma. The issue of ion sampling problems is discussed by Helm et al. (1980). However, it is the opinion of this author that mass spectroscopy (using extractive probes) has yet to be fully utilized in plasma processing, and that it will play a role in studies of discharge chemistry. One reason for this optimism is that similar problems exist in the application of MS to other chemically reacting systems, and there is evidence that it is possible to overcome these problems if precautions are taken. Sampling of reactive species will continue to be difficult, but it seems that MS can play a key role in providing spatially resolved profiles of stable species.

Perhaps the most widely studied system in plasma chemistry is silane decomposition for the deposition of amorphous silicon films (a-Si:H). Nolet (1975) measured silane decomposition kinetics in a DC flow discharge using a mass spectrometer with a pinhole sampling. Turban et al. (1979, 1980, 1982) studied silane decomposition of RF glow discharges, measuring both neutral and ionic species using mass spectrometry with sampling through an orifice (200 μm). Haller (1980) measured ionic species using pinhole sampling and quadrupole mass spectrometry in RF discharges in pure silane. Radicals were the focus of the study of Robertson et al. (1983) of DC discharges in mixtures of silane and argon. Line-of-sight sampling through an orifice was also used in this study. Reactive molecular fragments were distinguished from cracking products of stable species by controlling ionizing electron beam energy. (Reactive intermediates typically have 2–4 eV lower ionization thresholds than stable species). Longeway et al. (1984) used mass spectrometry to measure the time dependence of silane, disilane, and trisilane concentrations in a static DC discharge in silane. Many conclusions of these studies are summarized by Turban (1984) and so will not be repeated here. One feature of all the studies reported is the use of line-of-sight sampling through orifices in walls or electrodes. As a result, spatial profiles of species concentrations were not obtained.

When sampling ions, it is not necessary to use the ionizer in order to see a signal. This is used to discriminate the ion signal from the larger neutral signal. Ion sampling from the negative glow and positive column of various gases was investigated by Knewstubb and Tickner (1962a, b, c). More recently, interest has focused on ion sampling from RF discharges. Kohler et al. (1985a, b) measured ion energies using a spherical energy analyzer and quadrupole mass filter in low-pressure argon discharges. The purpose of these studies was to determine time-averaged plasma potential from measured ion energy as a function of power, plasma mode, and frequency. The simple capacitive sheath model of the RF glow discharge was tested and found to be valid for many of the conditions tested. Briaud et al. (1986) measured ion energy distributions from ions sampled through a 50 μm electrode orifice with a cylindrical energy analyzer (apparently no mass filter was used). The effect of frequency, pressure, and gas composition on the ion energy distribution was investigated and interpreted (primarily) in terms of secondary electron ionization and collisions in the sheath.

A popular technique for the study of reactive species kinetics is the flowing afterglow. In this method, gas flows through a discharge, is dissociated to some degree, then flows out of the discharge through a relatively long tube. Another gas may be added and mixed with the original gas, and it too may have been sent through a discharge. The rate of reaction is monitored by measuring concentrations as a function of mixing time and other parameters such as pressure, bath gas, and so on. Mixing time, or residence time, is controlled by varying gas flow rate with a fixed distance between the mixing point and measuring point. One complication is surface reaction on flow tube walls; typically, some form of passivation is used to reduce the rate of surface reaction. Also, usually a single species reaction is to be studied, and complications can arise if more than one other species is present. However, conditions can often be chosen such that a single free radical reacts with another species (present in excess to make the kinetics pseudofirst order), in order to avoid having to account for more than one reaction at a time. This can require a certain amount of cleverness in choosing the appropriate starting gases.

Examples of flowing afterglow/mass spectrometry studies include the work of Smolinsky and Flamm (1979) and a series of papers by Ryan and Plumb (1982; 1984a,b; 1986). Both sets of authors studied various aspects of plasma fluorocarbon radical chemistry. Smolinsky and Flamm (1979) examined CF_4 and CF_4-O_2 plasmas, measuring reaction products as function of conditions: pressure, power, O_2 content, and presence or absence of single crystal silicon. Similar downstream studies were performed by Flamm et al. (1979) for the reaction of fluorine atoms with SiO_2 and by Flamm et al. (1981) for the reaction of fluorine atoms with single-crystal silicon; in both studies, etch rate was reported as a function of F atom concentration, which was in turn measured using gas phase titration with Cl_2.

Ryan and Plumb (1982) studied the reaction of CF_3 radicals with O atoms. In order to measure the rate of loss of CF_3 radicals directly, it was necessary to ensure that the reaction mixture contained an excess of O atoms and relatively few CF_3 radicals in a bath gas of (primarily) helium. Measurements of the rate of decay of CF_3 vs. O atom density were used to obtain an estimate of the elementary reaction rate coefficient for this radical-radical reaction. A simplified diagram of the experiment is shown in Figure 13 (Plumb and Ryan, 1981). Gas flows into the system through inlet ports (designated *I* in the figure), through microwave discharges (designated *D1, D2*) in which dissociation takes place, then into mixing regions. The mixture flows past the mass spectrometer sampling port, then flows into the exhaust. The same apparatus was used by these authors to study the kinetics of: CF_3 and CF_2 with H atoms (Ryan and Plumb; 1984a); CF_2 with $O(^3P)$ to produce COF (Ryan and Plumb; 1984b); and CF_3 and CF_2 with F atoms and F_2 (Plumb and Ryan; 1986a). Although such measurements have been used in other research areas involving chemical kinetics (Fontijn and Clyne; 1983), these tools have only recently been applied to chemistries of interest in plasma processing. An example of an afterglow kinetic study in a system of interest industrially is the work of Danner and Hess (1986). These authors studied the etching of aluminum by chlorine atoms and undissociated mole-

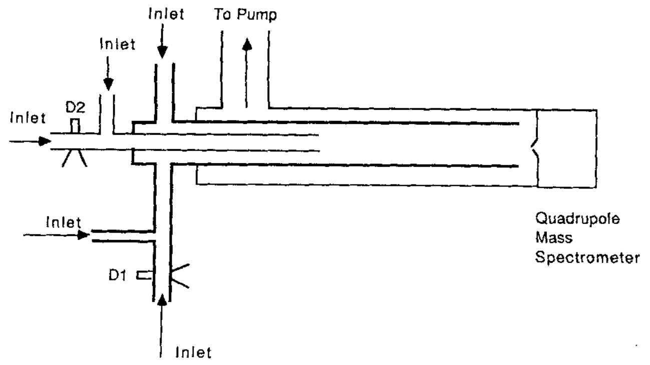


Figure 13. Flowing afterglow apparatus to measure elementary gas phase rate coefficients (after Ryan and Plumb, 1981).

cules (after the native oxide was removed). Gas phase concentration of Cl atoms was measured above the etch surface utilizing gas phase titration (via chemiluminescence) of NOCl. It was found that molecular chlorine etches aluminum at least four times faster than chlorine atoms. This result was attributed to a higher sticking coefficient for molecular chlorine compared to the atom.

The flowing or pulsed afterglow technique combined with mass spectrometry has been employed in studies of ion-neutral, ion-ion, and ion-electron reactions. The motivation for much of this work has, until recently, been the desire to understand planetary atmospheric phenomena, instellar chemistry (astrochemistry), and gas discharge lasers, all of which depend on ion chemistry. Smith and Adams (1981, 1984) and Lindinger et al. (1984) describe the history and current efforts in this field, with many references to the original literature. In a related paper, Smith and Adams (1984) discuss the interaction of charged particles in plasma chemical processes. Although ions are present at relatively low concentrations in weakly ionized plasmas, the fact that ion-neutral reactions are often very fast (ion-dipole interactions promote reaction) can mean that ions play an important role in neutral chemistry. Certainly, ion-neutral reactions can control the charged particle composition in the plasma, and this alone makes these reactions important.

Langmuir probes

There are many reviews of electrostatic probes, including several monographs. These include Swift and Schwar (1969), Chung et al. (1975), and Chen (1965). Only the most rudimentary principles of probe theory and practice will be discussed here; for more details the reader is referred to the cited monographs and the many references contained therein.

This technique involves insertion of a conducting probe (a thin cylindrical wire, for example) into the plasma, the application of a potential to the probe, and measurement of the resulting current. From the shape of the voltage-current characteristic, and the use of a model of the probe response, one can (in principle) determine the density and energy of ions and electrons and the local plasma potential. Although this method is very simple to implement, there are a series of problems. The first is the problem of the probe disturbing the local plasma environment. Second, proper interpretation of the voltage-current characteristic can be difficult. In processing plasmas, additional problems include probe surface contamination and interpretation of probe response in RF plasmas.

Probes give no information on neutral chemistry in the discharge, and do not readily distinguish between ions of different composition. However, at least in principle, probes can provide spatially resolved profiles of discharge electrical properties and this is important in understanding discharge chemistry. Because of the difficulty in probe interpretation, some plasma processing analysts view probe data with suspicion. The problems notwithstanding, it seems likely that as understanding of processing plasmas progresses and it becomes clearer when probe results can be trusted (and when comparisons to other, less perturbing techniques are made), probes will be used routinely to help characterize processing plasmas.

Discharge chemistry modeling

The discussion in this section will focus on several modeling studies of flowing afterglows. These particular studies were chosen partly because they each contain meaningful comparisons to experimental measurements of chemical species. In addition, the fact that current models of discharge physical structure are rudimentary suggests that models that minimize the importance of the active discharge will be most useful. Each of the models is based on the experimental measurements of Smolinsky and Flamm (1979), in which mass spectrometric analyses were made of the reaction products from a flowing afterglow of CF_4 and CF_4-O_2 plasmas. In some experiments, single-crystal silicon was added to include silicon etching reactions. Species concentrations were measured as a function of residence time, inlet gas composition, and pressure.

In the first model (Edelson and Flamm, 1984), a one-dimensional plug flow model was used, with a plasma section followed by an afterglow section. In the plasma section, a constant electron and ion density of 10^{10} cm^{-3} was assumed, and electron temperature was taken to be 5 eV. Gas phase and surface reactions were included in the model, including surface polymerization reactions. Adjustable parameters were used for sticking coefficients, surface recombination rates, and surface polymerization rates. A sensitivity analysis of model results was made and the conclusions were that transport processes, surface chemistry, and formation of fluorocarbon polymer films are dominant processes. Agreement between model results and experimental measurements was fair, but the major difficulty with assessing the model validity is in its complexity. There are so many parts of the model which could be responsible for causing the differences between observed and predicted results that it is difficult to say with confidence what parts worked well and what parts need improvement. The sensitivity analysis was intended to help provide this information, but sensitivity analyses are limited by the mechanisms and assumptions in the model: they provide good information about what mattered in that particular model, but little information is provided about the validity of model assumptions.

Models developed by Plumb and Ryan (1986b) and Ryan and Plumb (1986) have the advantage that emphasis was placed on gas phase reactions and adjustable parameters were not used. As a result, it is possible to see how well only gas phase chemistry is able to account for the observed results, in terms of previously determined rate coefficients. In addition, these authors point out that most of the chemistry can be represented by rela-

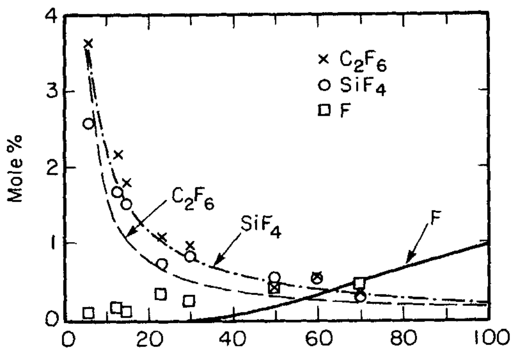


Figure 14. Comparison of flowing afterglow measurements of Smolinsky and Flamm (1979) and model of Ryan and Plumb (1986) for a CF_4 plasma etching silicon.

Symbols: measured downstream concentrations of C_2F_6, SiF_4, and F atoms as a function of total flow rate
Lines: model predictions

tively few reactions: 13 reactions (from an original set of 49) in the case of CF_4-O_2 plasmas, and nine reactions (from an original set of 20) for CF_4-Si plasmas. It was found that agreement between predicted and measured stable species profiles agreed to within a factor of 2 over wide ranges of experimental conditions, and this was taken as evidence that the chemistry in fluorocarbon etching plasmas is dominated by gas phase radical reactions. A representative comparison of model predictions and experimental results is shown in Figure 14. It can be seen that measured and predicted downstream concentrations agree fairly well over a wide range of flow rates.

One strength of flowing afterglow models is that they do not rely on discharge structure models, which are rudimentary at present. Another strength is that the configuration lends itself to a relatively simple treatment of flow and transport properties of the reacting species: a one-dimensional treatment is usually satisfactory. The flowing afterglow has emerged as the most popular configuration for the study of plasma chemistry because of these advantages. However, ultimately we are interested in modeling the discharge itself, and this will involve a more complex system in which (among other things) spatial variations are usually important. Since gradients often exist near electrode surfaces, spatial variation must be accounted for in realistic models. A related area in which chemically reacting weakly ionized gases have been modeled is gas discharge lasers (Smith and Thompson, 1978). Another field with a considerable history of modeling is gas discharge lamps. However, in many cases for both lasers and lamps, one is interested in the DC positive column region, in which axial gradients can be neglected. Radial variations are relatively mild and can often be averaged. Thus modeling typically involves spatial averages, which allows a much more detailed treatment of electron, ion, and neutral species dynamics and chemistry. As a result, many of the modeling approaches taken in discharge lamp or laser analysis are impractical for plasma process modeling in which spatial gradients must be included.

In validating models with spatial gradients, it is necessary to compare spatial profiles of reacting species to model predictions. In the work of Breiland et al. (1986a, b), laser spectroscopy (LIF and spontaneous Raman) was used to map profiles of SiH_4, Si, and Si_2 in a silane CVD reactor. A representative comparison between Si atom profiles (measured by LIF) and fundamental model predictions as a function of susceptor temperature is presented in Figure 15. The qualitative agreement between predictions and measurements suggests that the model of chemistry and transport is fairly satisfactory. The major requirements for similar results for plasma reactor models are development of reliable models of discharge physics, and a better understanding of surface processes. The former requirement has been discussed already, the latter is the topic of the next section.

Surface processes

The importance of surface processes in plasma reactors is obvious since the result of plasma processing is a modified surface. However, it is equally clear that surfaces are manipulated in plasma processing primarily through gas phase mechanisms. The neutral reactants responsible for surface chemistry are created mainly by gas phase electron impact dissociation, and ions bombard surfaces due to the presence of the gas phase plasma. Complicating matters further is the coupling that exists between gas and surface chemistry: species created at surfaces can desorb into the gas phase and modify gas phase chemistry and discharge physical structure. This is commonly observed in etching since etch products must be pumped away. It is generally accepted that plasma chemical (and physical) processes are sensitive to the nature of surfaces bounding the plasma.

The coupling between gas phase and surface processes in plasmas, the incomplete understanding of gas phase processes, and the general difficulty of *in situ* plasma surface measurements combine to make the problem of systematic plasma surface studies difficult in discharges. As a result, most studies of plasma surface phenomena have been conducted outside the discharge. Two approaches have been taken:

1. Downstream, afterglow studies (Flamm et al., 1981)
2. High vacuum studies (Coburn et al., 1977; Coburn and Winters, 1979; Tu et al., 1981; Vasile and Stevie, 1982; McNevin and Becker, 1985)

High vacuum studies have been pursued because of the advantages of greater control over the species interacting with the surface, and the greater number and quality of surface diagnostic tools available under high vacuum conditions. The main disadvantage of *ex situ* studies is that conclusions drawn from

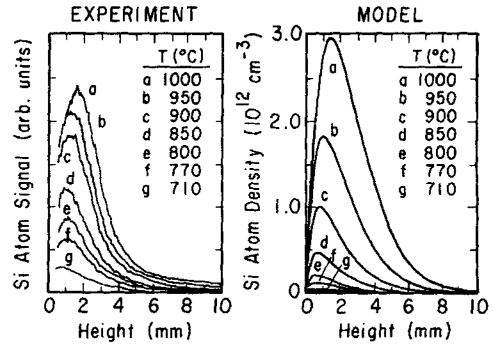


Figure 15. Experimental measurements of Si atom spatial profiles in a thermal chemical vapor deposition reactor, compared to model predictions for a series of surface temperatures (Breiland et al., 1986b).

idealized environments may be misleading when applied to the more complex plasma systems of industrial interest.

Etching systems have received the most attention to date, and most of these studies have concentrated on silicon-containing surfaces being etched by fluorine-containing compounds. Coburn and Winters (1979), in a now classic paper, first clearly demonstrated the synergistic importance of ion bombardment in the presence of neutral reactants in etching. In Figure 16, a diagram of their experimental apparatus is shown. Both ions (from an ion source) and neutral species were directed independently at the surface to be etched. In order to measure etching rate *in situ,* a quartz crystal microbalance (QCM; Warner, 1969; Coburn, 1984) was used.

The key result is shown in Figure 17. Plotted is silicon etch rate vs. time for three conditions:

- Application of only XeF_2 (a convenient fluorine-containing gas) to the surface
- Application of both gas and Ar^+ ion beam to the surface
- Application of only the ion beam to the surface

Clearly, the maximum etch rate depends upon the presence of both neutral gas and ion bombardment. With only neutral gas, dissociative chemisorption followed by surface fluorination of silicon and subsequent desorption of a volatile silicon fluoride was responsible for etching. With only the ion beam, physical sputtering accounts for the small but nonzero etch rate. Together, energy from the ion beam and the presence of the chemically active neutral gas enhances the overall rate of etching.

The exact mechanism by which the ion beam enhances the rate of chemical etching is still not completely understood. Etching requires a sequence of events: adsorption of neutral reactants in some form, chemical reaction with the film, then desorption of the volatile product. Ion bombardment could increase the rates of any or all of these processes. Unfortunately, it is difficult to devise experiments that are capable of unambiguously discriminating between the different possibilities.

There have been a number of reviews in recent years that address many of the fundamental issues involved with surface processes in reactive plasmas (Coburn and Winters, 1983, 1985; Winters et al., 1983; Hess, 1986). Among the observations and conclusions are:

1. Although it is possible that electron and photon bombardment play a role in enhancing surface processes, ions appear to be the dominant form of radiation in most cases.

2. In some systems (e.g., Si etched by fluorine or chlorine species), ion bombardment results in a large increase in etching rate, but in other systems there is no appreciable effect (e.g., Al etched in Cl_2), and in still others ion bombardment actually reduces etching rates (Cu etched in Cl_2 above 200°C).

3. Ion bombardment is usually necessary (but not always sufficient) to promote anisotropic etching. Exactly how ion bombardment induces anisotropic etching is not completely clear, but the effect must be related to a net increase in etching rate at trench bottoms compared to sidewalls. This could be due to enhanced rates of gas-surface chemistry at trench bottoms, or the presence of condensible species in the plasma may act to coat trench sidewalls and bottoms. Ion bombardment enhancement of anisotropy in this case could be due to physical or chemical sputtering of the etch-inhibiting layer at the trench bottom but not along sidewalls.

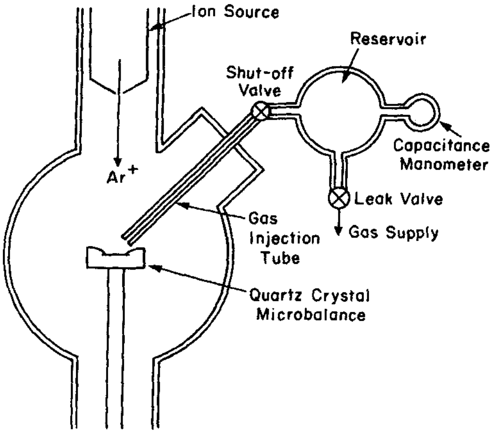


Figure 16. Apparatus used (Coburn and Winters, 1979) in study of synergism between neutral surface chemistry and ion bombardment in plasma etching.

4. One proposed mechanism for ion-enhanced surface processes is that ions act primarily to promote the rate of surface reaction rather than reactant adsorption or product desorption. For example, a tightly bound layer (SiF_x or SiCl) covers the entire surface, and weakly bound precursors (F or Cl) are physisorbed in low concentration on this layer. The precursors can react with the underlying layer only when energy sufficient to promote the tightly bound species to an excited state is provided by a bombarding ion. When this occurs, a saturated species is created (SiF_4 or $SiCl_4$) and it spontaneously desorbs due to its relatively high vapor pressure at typical surface temperatures. The precursor state has been proposed to account for the commonly observed weak dependence of reaction rate on surface coverage, and is an idea that has a long history in surface chemistry studies (Winters et al., 1983, and references therein). It has been observed that fluorinated silicon that has been left in vacuum for long periods of time (so no weakly bound F is present) also shows very large ion-assisted etch yields (J.W. Coburn, personal communication, 1988). This implies that some mechanism such as disproportionation is occurring to create SiF_4 from the partially fluorinated layer.

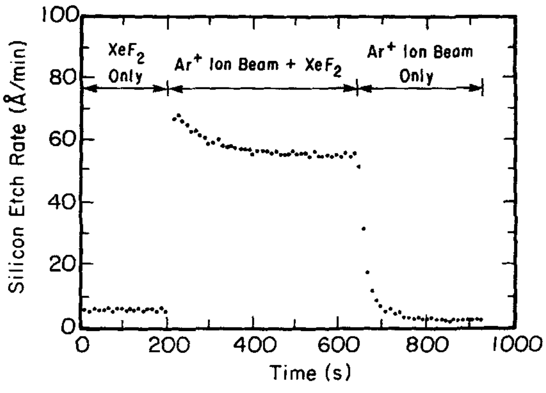


Figure 17. Either neutral etching only (via F-atom source XeF_2) or ion bombardment only yields low etch rates, but the two together result in a large etch rate (Coburn and Winters, 1979).

5. Another possibly important mechanism in spontaneous etching (where ion bombardment is not required) is the formation of negative ions at the surface followed by field-assisted penetration into the lattice. In support of this hypothesis, it has been observed that silicon heavily doped with *n*-type material (which increases the availability of electrons) displays fast and spontaneous etching in chlorine- and bromine-containing plasmas.

A particularly noteworthy series of fundamental measurements related to etching mechanisms have been reported by McFeely and coworkers (Morar et al., 1984; McFeely, 1985; McFeely et al., 1986). These workers used photoemission spectroscopy (*ex-situ,* UHV studies) to infer the surface bonding characteristics of surface fluorosilyls involved in fluorine etching of silicon. They discovered that the surface species resulting from only chemisorption and no steady-state etching of silicon were very different from those observed after steady etching. In the former case, surface modification is confined to the first monolayer, whereas in the latter case, a reaction layer about 7–10 monolayers thick is formed. The most common surface species observed was trifluorosilyl (SiF_3) in the post-steady-state etched surfaces. In addition, SiF_4 was observed in varying concentrations (depending on the reaction pressure used) for the post-steady-state etched surfaces.

Although considerable fundamental research has been conducted and will undoubtedly continue on surface mechanisms involved in film etching and deposition, there remain many pressing needs. From the point of view of macroscopic modeling, a relationship between etch (deposition) rate and such variables as ion and neutral composition, flux, and energy is needed. It probably is not legitimate to separate the effects of ion bombardment and neutral flux on surface chemistry, but there seems to have been little work that would suggest the proper form of a surface chemical rate enhancement factor. Even semiempirical expressions that capture the most important aspects of surface physics and chemistry would be a valuable first step.

Concluding Remarks

Plasma processing in microelectronics manufacturing and related industries is thriving and promises to continue to be an important technology. Chemical engineers should be able to make substantial contributions to refinement of the technology because of the nature of the problems involved: complex chemically reacting flows that must be carefully controlled to achieve desired process objectives. However, it is essential that chemical engineers become familiar with the principles of discharge physics and the nature of the product to be produced: modified surfaces and thin films to be processed further in the manufacture of electronic or optoelectronic devices.

Much has been learned from empirical studies of which gases (and mixtures) will etch or deposit films under a variety of conditions and in different reactor designs. Empirical and semiempirical methods will remain useful for process development and design for the foreseeable future. However, it is clear that continued improvement in the technology will require a better understanding of underlying discharge physics and chemistry, and the relation of these to surface characteristics. Development of this understanding will require systematic studies of gas phase and surface chemical processes both in the presence and absence of a discharge. In systems with the degree of coupling observed in plasma chemical reactors, detailed mathematical models are essential to develop process insight. In a variety of other fields with similar chemical and physical complexities (combustion, atmospheric chemistry, chemical vapor deposition), the combination of spatially resolved spectroscopies (laser spectroscopy in particular) and detailed mathematical models has been successful in elucidating gas phase mechanisms. There is every reason to expect that a similar strategy will yield analogous results in plasma processing. However, a major problem in this and all other surface processing technologies is the development and application of diagnostics and models of processes occurring at surfaces. It seems clear that the coupling between gas phase and surface physics and chemistry, then between surface processes and surface properties will be a daunting challenge for many years.

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Notation

A = constant
E = electric field strength
e = charge on electron
f = electron energy distribution function
h = Plank's constant
I = current
j = particle flux
k = Boltzmann's constant
$k_{\text{subscript}}$ = rate coefficient
L = electrode separation
M = mass (heavy particle)
m = mass (light particle)
n = number density
R = resistance
$R_{\text{subscript}}$ = rate
T = temperature
V = voltage
x = position

Greek letters

α = Townsend first ionization coefficient (defined as gas phase ionization rate coefficient divided by local drift velocity)
γ = Townsend second ionization coefficient; constant of proportionality between rate of secondary electron emission from surface and ion flux at surface; i.e., (j_e) secondary $= -\gamma j_+$
δ = fraction of energy transferred between electron and heavy particle in elastic collision
ϵ = electron energy
ϵ_0 = permitivity of free space
λ_D = Debye length
μ = mobility
ν = frequency of emitted photon
σ = collision cross section

Subscripts

e = electron
$+$ = positive ion
i = ionization
ext = excitation
x = ground state

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