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CHEMICAL VAPOR DEPOSITION

Thermal and Plasma Deposition of Electronic Materials

S. SIVARAM

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Chapter 6

Fundamentals of Plasma Chemistry

Up to now we have considered CVD processes in which the source of energy for the forward process of endothermic reactions was purely thermal. However, interactions involving charged particles produced in a plasma have been effectively utilized in various CVD processes to reduce reaction temperatures. Figure 6.1 illustrates the familiar energy diagram for a reaction: reaction pathway X is the one we have previously considered in thermal CVD, where the forward reaction between reactants A and B has to overcome the potential hill, corresponding to an activation energy. However, the presence of charged particles opens up new reaction pathways such as Y, with a lower activation energy.[1] The lowering of the activation energy through the formation of excited species A^* and B^* allows the forward reaction to proceed at lower substrate temperatures or at increased rates for the same temperature when compared with thermal CVD.

The need for lowering the temperature in IC processing arises from many requirements. For example, in an integrated circuit, once aluminum-based metallization has been deposited and patterned, the highest allowable processing temperature for the wafer is constrained below the melting point of the aluminum alloy (about 650°C). In most cases, due to other diffusive processes at temperatures close to the melting point of aluminum, operating temperatures have to be maintained below 450°C.

The use of a plasma also provides other advantages. For instance, energetic charged particle collisions can produce metastable species (such as C^* in Figure 6.1), new reaction paths and produce species not available through thermal CVD; control of film microstructure and mechanical properties can be enhanced through ion bombardment; and directionality in film deposition

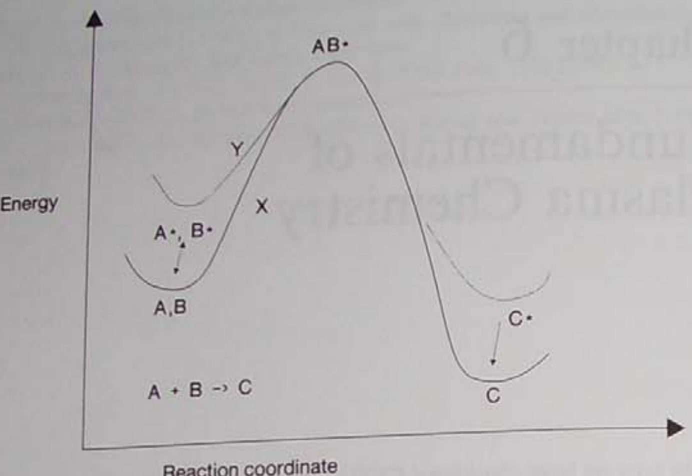


FIGURE 6.1. Energy change and species formed (X) with a thermal CVD path and (Y) with a plasma CVD path. The plasma reduces the activation energy.

and etching can be achieved through the acceleration of charged species in a directional potential gradient.

In this chapter we consider the fundamentals of plasma chemistry by focusing on the interactions between electrons, ions and neutrals in a discharge. We do this from a physical viewpoint and from the viewpoint of chemical reactions between them. Chapter 7 will focus on the production and sustenance of processing plasmas in commercial CVD reactors optimized for thin film deposition.

6.1. BASICS OF PLASMAS

Let us begin with a definition:

> A plasma is a quasi-neutral gas of charged and neutral particles which exhibits collective behavior.

What we mean by *quasi-neutral* and *collective behavior* will become clear shortly. In this section we study the behavior of a plasma in the following sequence:

a. Understanding the constituents of a plasma, their relative concentrations and energies.

b. Since the plasma contains charged species, we develop expressions for plasma potential with reference to the confining walls and the substrate.
c. Understanding the collective behavior of the plasma under external perturbations.

6.1.1. Physical Characteristics of Plasmas

Any body of gas typically contains three species: neutral atoms or molecules, ions and electrons. Their relative concentrations (i.e., the degree of ionization) are considerably different in a plasma. The concentration of ions in the atmosphere is negligibly small. In a typical glow discharge plasma used in CVD processes, ionic concentrations are of the order of 10^{10} per cm^3. The electron concentration is the same as the ion concentration, so the overall plasma is electrically neutral.

From fundamental kinetic theory, the kinetic energy of a particle is given by

$$\varepsilon = \tfrac{1}{2}mv^2 \tag{6.1}$$

If we substitute the Maxwellian velocity distribution into the right-hand side of equation (6.1) after some algebraic manipulation, we can derive the average energy of the gas phase as

$$\bar{\varepsilon} = \frac{\int \varepsilon n(\varepsilon)d\varepsilon}{\int n(\varepsilon)d\varepsilon} = \frac{3}{2}kT \tag{6.2}$$

If we extended equation (6.2) which was derived for neutral atoms and molecules, to include electrons and ions, we can see that the energies of electrons and ions can be represented in terms of a temperature. And in a plasma the electrons and ions can have different velocity distributions (or energy distributions) so there can be many different temperatures in a plasma. Typically, in glow discharge plasmas the electron temperatures are on the order of 1–10 eV (10 000–100 000 K), and the ion temperatures are on the order of 0.1 eV (1 000 K). The temperature of neutrals is similar to the ion temperature and is indicated by more routine temperature measurements.

Figure 6.2 illustrates some characteristics of plasmas, including those that occur naturally (terrestrial and celestial), and some that are artificial.[2] The portion relevant to CVD processing occurs in a region known as *glow discharge*. The term glow discharge arises because atoms excited by electron impact release energy in the form of photons when they relax; the photons produce the glow. The degree of ionization in each of the different plasmas

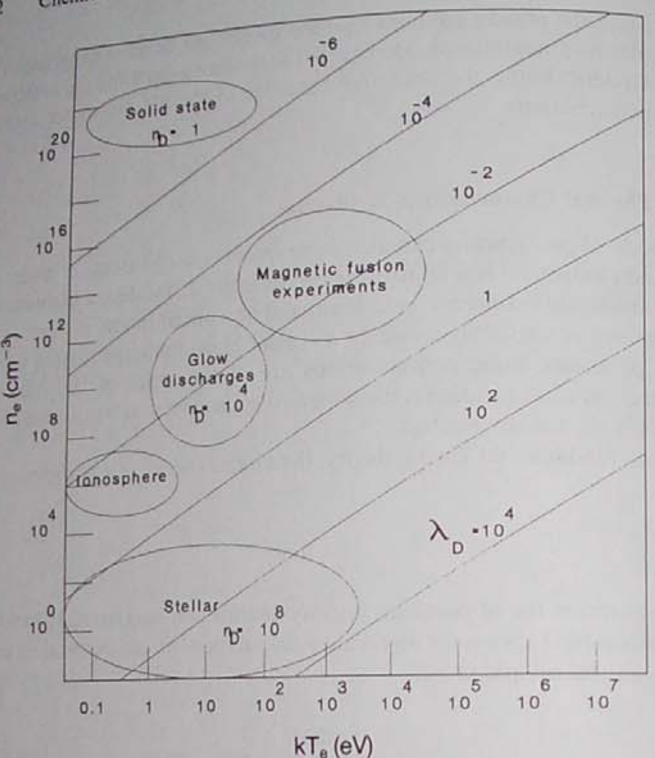


FIGURE 6.2. General characteristics of some natural and man-made plasmas. The illustrated parameters are discussed in the text. λ_D = Debye length (cm) and n_D = the number of electrons in a Debye sphere (order of magnitude). Adapted from Ref. 2 with permission from John Wiley & Sons.

is also shown. Table 6.1 summarizes properties of a typical glow discharge used in CVD reactors. Throughout the rest of this book, the terms plasma, glow discharge and discharge are used loosely and interchangeably. In all cases we refer to the region in Figure 6.2 marked as glow discharge plasma.

An understanding of the interactions between the three types of species and the energetics involved in these processes is essential for us to make use of plasmas in producing thin films. Energy transfer into a plasma and between the species, diffusional phenomena within the plasma and chemical reactions in the presence of charge species are some of the processes that depend on collisions between the three species.

TABLE 6.1 Properties of a Typical Glow Discharge

Electron concentration	10^{10} to 10^{11} per cm^3
Ion concentration	10^{10} to 10^{11} per cm^3
Electron temperature	3–5 eV
Ion temperature	0.05 eV
Debye length	0.1 cm
Electron velocity	10^7 cm/s
Ion velocity	10^4 cm/s

6.1.2. Collisional Processes in a Plasma

In a field-free space, charged particles behave the same way as neutrals, and their behavior can be treated similarly using the kinetic theory of gases. Collisions between particles can be written in terms of a mean free path λ given by

$$\lambda = \frac{1}{\sqrt{2}n\sigma} \tag{6.3}$$

where n is the number density of the particles and σ is the collision cross section. The collision cross section is a measure of the probability that a collision process between the particles in question will occur. Even though the process might be more complicated than the collision of two hard spheres, similar to billiard balls, the collision cross section retains the unit of area. For electrons, the collision cross section is a small number; ions, which are large and more massive, have larger collision cross sections. Electron–electron collisions dominate when the degree of ionization exceeds 10^{-4} or 10^{-3}, i.e., $n_e = n_i > 10^{15}$ per cm^3, seldom seen in processing plasmas.

The mass difference between the electron and the ion is manifested as a difference in their respective accelerations in the presence of a field. The acceleration of a charged particle in an electric field is given by

$$m\frac{dv}{dt} = -ZeE \tag{6.4}$$

where dv/dt is the acceleration of a particle with mass m. Z is the number of charges on the particle and e is the electronic charge. Note that the electric field E is always *as felt* by the charged particle, irrespective of the applied field. For instance, in the parallel-plate diode shown in Figure 6.3, the electron paths from the cathode to the anode are a function of the current density. At a high current density, existence of other electrons in the proximity of a

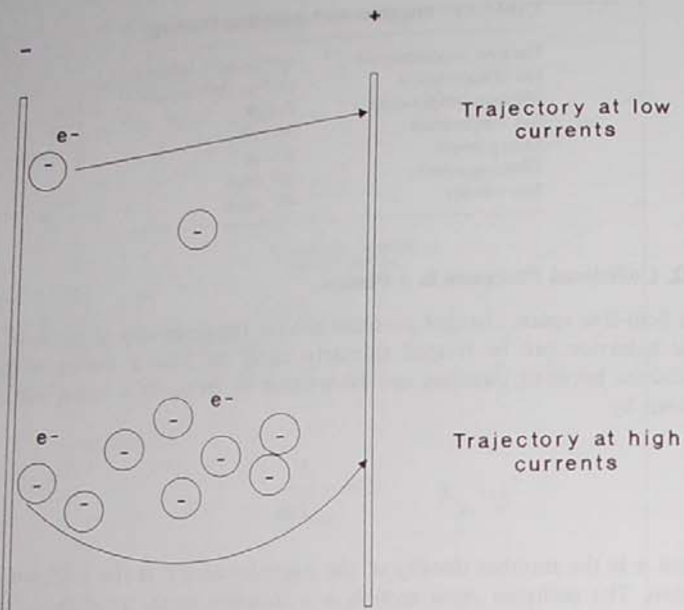


FIGURE 6.3. The electron path from the cathode to the anode depends on the spare charge, the charge density that screens some of the potential.

particular electron can completely shield it from the anode, resulting in a curved trajectory. The shielding electrons are called space charge and we will be studying its effect when we deal with many plasma properties.

Due to their small mass electrons acquire kinetic energy from the electric field much more rapidly than ions, hence energy from an electric field is coupled to a gas entirely through the kinetic energy of electrons. Electrons in turn lose their energy by collisional processes with ions and neutral species present in the gas phase. However, from the classical theory of elastic collisions, the elastic energy transfer per two-body collision (as in a collision between an electron and a neutral/ion) is given by $2m/M$ where m and M are the mass of an electron and neutral/ion respectively. Since m can be more than three orders of magnitude smaller than M, the fractional energy loss per elastic collision between an electron and a massive ion or a neutral particle is negligible.

Inelastic processes, those in which kinetic energy is not conserved, are the primary means through which the externally applied field accelerates electrons

and transfers energy to other species in the plasma. Such processes include impact ionization, electron attachment and chemical processes in the gas phase. We will treat them in more detail when we address issues relating to reactions in the plasma. These processes make up the fundamentals of plasma chemistry and their effective application directly contributes to the usefulness of CVD plasmas.

Exercise 6.1

What is the velocity of a 15 eV electron? What is its temperature in Kelvin? If its collision cross section with an Ar atom is 2.5×10^{-15} cm^2, what is the probability it will collide with an Ar atom when it travels a distance of 1 cm. The chamber pressure is 10 millitorr.

6.2. PLASMA POTENTIAL

In our earlier definition of a plasma, we used the terms quasi-neutrality and collective behavior without dwelling on their true implications. We will develop our understanding of these terms by examining the perturbation caused by a CVD substrate. If the substrate is grounded, it can be considered as similar to the grounded walls confining the plasma. If it is left floating, it assumes a potential V_f. Let us examine the relationship between the potential of the plasma V_p and the potential of an electrically isolated surface, V_f, before considering the case of the grounded substrate.

6.2.1. Electrically Isolated Surface in a Plasma

The impingement rate of any particle arriving at a surface was calculated in Chapter 2 from the kinetic theory of gases. For the arrival of charged particles at the electrically isolated surface, the flux can be modified to a current density J by multiplying the charge carried by the species.[3]

$$J = \frac{ne\bar{v}}{4} \tag{6.5}$$

where n is the density of charged species and $\bar{v}$ is the average velocity of charged species arriving in a random fashion from the bulk of the plasma. Electron velocities in a plasma are much higher than the ion velocities; this is because the electron has a smaller mass (Table 6.1). As a result the electron current arriving at the floating substrate is initially larger than the ion current. The substrate becomes negatively charged and starts to repel further electron flux.

Since the region around the substrate is depleted in electrons, there are fewer collisions between electrons and ions, hence less glow. This region is called the dark space or sheath. Even though the plasma as a whole (including the dark space) is neutral, the local densities of ions and electrons can be different, especially around a point of disturbance. This is the origin of the term quasi-neutrality.

Since V_f acts to repel electrons, by convention it is smaller than V_p. Since electron velocities are always larger than ion velocities, we can generalize this conclusion and state that "the plasma potential is more positive than any potential exposed to the plasma".[4] As there is no other reference potential, $V_p - V_f$ is the only meaningful parameter we can model.

The immediate region around the substrate gets depleted of electrons and has a higher density of positively charged ions. Only those electrons in the body of the plasma that possess energies larger than the repulsive barrier can get through to the substrate. From the Maxwell–Boltzmann distribution, the number of electrons, n_f, out of the electron density n_e, with sufficient energy to overcome the potential hill $V_p - V_f$ is given by

$$\frac{n_f}{n_e} = \exp[-e(V_p - V_f)/kT_e] \tag{6.6}$$

At steady-state conditions, the electron and ion fluxes have to be equal. So, we can individually write out the two fluxes and equate them to calculate $V_p - V_f$.

$$V_p - V_f = \frac{kT_e}{2e} \ln \frac{m_i T_e}{m_e T_i} \tag{6.7}$$

Thus electron and ion temperatures in the plasma and the mass of the ion determine the potential of a floating substrate with respect to the plasma. Conversely, measurement of this potential difference provides a means of measuring electron temperature, as we will see in our discussion of the Langmuir probe in Section 6.4.

6.2.2. Nonisolated Surface in a Plasma

We can also derive an expression for the current through the sheath if the substrate were made conducting, as in the case of a grounded wall or a conducting cathode. And we can calculate the current when conduction is limited by the space charge in the sheath.[5] Intuitively, it would be a function of sheath width d and voltage V across the sheath. Let us consider an

electrode at a large negative potential V, similar to a cathode in a DC discharge. Since there is a large negative potential let us ignore the electron current and assume no electrons in the sheath. Current density J at any instant is given by

$$J = nev \tag{6.8}$$

where v is the instantaneous velocity of the ions, in contrast to the electron flux in equation (6.5), the result of random arrival of electrons at an isolated surface. The change in voltage across the sheath can be expressed in terms of Poisson's equation as

$$\frac{d^2V}{dx^2} = -\frac{ne}{\varepsilon} \tag{6.9}$$

where ε is the permittivity. Also the kinetic energy of the ions due to acceleration in the field can be written as

$$\frac{mv^2}{2} = eV \tag{6.10}$$

Eliminating v from the previous two equations, we can write

$$\frac{d^2V}{dx^2} = \frac{1}{\varepsilon}\sqrt{\frac{m}{2eV}} \tag{6.11}$$

The solution to maximum space charge limited current from equation (6.11) is given by

$$j_{\max} = \frac{4\varepsilon\sqrt{2\frac{e}{m}V^3}}{9d^2} \tag{6.12}$$

Equation (6.12) gives the maximum current through the sheath when the current is limited by space charge; it is called Child's law. As we expected, the current through the electrode of a discharge or a grounded wall is a function of the voltage across the sheath V and the width of the sheath d. For a grounded wall the voltage is just the plasma potential; for a non grounded conduction electrode, the voltage depends on the applied potential.

6.2.3. Debye Shielding

Collective behavior arises because the plasma reacts to oppose an externally applied charge by forming sheaths. For instance, if an external battery is used to apply a potential V_c at location x_0 in a plasma, the plasma forms a sheath around the field so the effect of the applied potential is diminished at all locations away from x_0. The radial distance from x_0 at which the potential perturbation is reduced by a factor of $1/e$ (to approximately 37%) is known as the Debye length λ_D[6] and is given by

$$\lambda_D = \sqrt{\frac{\varepsilon_0 kT}{n_e e^2}} = 743\sqrt{\frac{T_e(\text{eV})}{n_e(\text{cm}^{-3})}} \tag{6.13}$$

The net effect of the Debye shielding phenomenon is that the plasma readjusts itself to attenuate any perturbation from the plasma potential. The plasma thus attempts to maintain a constant potential. Conversely, when attempting to study the effects of individual charged species, it is not necessary to consider coulombic interaction between the particle and its neighbors more than $2\lambda_D$ or $3\lambda_D$ away. For a typical glow discharge used in CVD, λ_D is on the order of a few hundred microns and sheath thicknesses are many times the Debye length. Debye lengths corresponding to the difference kinds of plasmas are noted in Figure 6.2.

The concentration of electrons inside a Debye sphere is a good estimation of the degree of ionization.[7] The number of electrons n_D inside a Debye sphere is given by

$$n_D = \frac{4\pi}{3}\lambda_D^3 n_e \tag{6.14}$$

$n_D \gg 1$ is often treated as a criterion for the definition of a plasma. Figure 6.2 also shows the number of electrons inside the Debye sphere for various plasmas.

Another implication of the Debye shielding phenomenon is the response of the plasma to alternating fields. The time it takes for an electron to move one Debye length, t_p is given by

$$t_p = \frac{\lambda_D}{v_e} \tag{6.15}$$

This is a reasonable estimate for the time it takes for the shielding to "get in place," i.e., the response time for the plasma to react to an external charge.

The inverse of t_p is called the plasma frequency, ω_p[8] and is given by

$$\omega_p = t_p^{-1} = 5.64 \times 10^4 \sqrt{n_e(\text{cm}^{-3})} \tag{6.16}$$

Collisions result in the damping of an applied electric field frequency, so the plasma remains static. However, when the applied field frequency exceeds the plasma frequency, the plasma is no longer able to shield the applied frequency, resulting in charged particle oscillations within the plasma.

6.2.4. Charge Diffusion in Plasmas

When considering reactor design for thermal CVD, we stressed the importance of low pressure CVD in enhancing the diffusion of reactant species. Diffusion of neutral species under a concentration gradient ∇n follows Fick's law

$$\Gamma = -D\nabla n \tag{6.17}$$

where Γ is the diffusional flux and D is the diffusion coefficient. However, the presence of charge on the diffusing species results in the diffusional flux being affected by space charge related fields, even if there is no external field gradient. For instance, in a plasma, since electrons in general are more mobile, diffusion of electrons along a concentration gradient leaves behind excess positive charge, resulting in a local field which acts to slow down further diffusion of electrons.[9] In discharges with charge concentrations $n_e > 10^3/\text{cm}^3$, the space charge related field $\mathbf{E}_{sc}$ becomes large enough such that the diffusional flux for electrons can be written as

$$\Gamma_e = -D_e\nabla n_e - n_e\mu_e\mathbf{E}_{sc} \tag{6.18}$$

where μ_e is the drift velocity of electrons in a unit electric field and $\mathbf{E}_{sc}$ is the space charge related field. Similarly, the flux for ions can be expressed as

$$\Gamma_i = -D_i\nabla n_i + n_i\mu_i\mathbf{E}_{sc} \tag{6.19}$$

where the subscript i denotes the corresponding quantities for a positive ion.

Let us examine each of the terms in equations (6.18) and (6.19) in turn. For a Maxwellian distribution of velocities and for collision frequencies that are independent of species velocity, the diffusion coefficient D can be related to temperature as

$$D_e = \frac{kT_e}{m\nu_e} \tag{6.20}$$

where v_e is the collision frequency. The mobility μ can be defined as

$$\mu_e = \frac{e}{m v_e} \tag{6.21}$$

The relationship between mobility and the diffusion coefficient for a Maxwellian velocity distribution is defined by Einstein's equation

$$\frac{D}{\mu} = \frac{kT_e}{e} \tag{6.22}$$

At a steady state, due to charge balance requirements, the fluxes of electrons and ions equalize, allowing us to solve for the unknown quantity $\mathbf{E}_{sc}$. Since $n_i = n_e$, and taking

$$\Gamma = \Gamma_e = \Gamma_i$$

we can arrive at an expression for $\mathbf{E}_{sc}$ by combining equations (6.18) through (6.22).

$$\mathbf{E}_{sc} = -\frac{(D_e - D_i)}{(\mu_e + \mu_i)} \frac{\nabla n}{n} \tag{6.23}$$

Substituting $\mathbf{E}_{sc}$ back into equation (6.18) results in

$$\Gamma = -\frac{(D_i\mu_e + D_e\mu_i)}{(\mu_e + \mu_i)} \nabla n \tag{6.24}$$

where D_a is called the ambipolar diffusion coefficient.[10] Ambipolar diffusion occurs in plasmas when the electron density is larger than 10^8 per cm^3, characteristic of most discharges used in CVD.

In a plasma CVD reactor with gradients in the species caused by flow, temperature, and species consumption effects, ambipolar diffusion plays an important role in determining the concentrations of reactant species at the substrate surface. Since chemical reaction rate is determined by surface concentration, diffusional terms are critical in the design of the reactor as we will see in the next Chapter.

6.2.5. Summary

We introduced the idea of temperature to indicate the energies of electrons and ions in a plasma. We saw the potential distribution in a system containing a plasma confined between grounded walls and in the presence of an isolated surface. The plasma is the most positive body in the system. We also derived expressions for current through a conductive electrode connected to ground or an external potential. And we looked at the plasma's ability to shield out external perturbations at frequencies up to the plasma frequency. Finally we saw the effect of the space charge related field in equalizing the diffusional fluxes of the ions and electrons, despite differences in their mobilities.

Exercise 6.2

In a nitrogen plasma where the neutrals are at room temperature, the average ion temperature is 0.05 eV and the electron temperature is 2 eV. The electron density is 2×10^9 per cm^3. If a floating surface is exposed to the plasma, what is the average energy of electron bombardment on the surface? At what distance from the perturbation will the plasma return to the plasma potential?

6.3. PLASMA CHEMISTRY

From the relative inefficiency of energy transfer through elastic collisions between electrons and ions or neutrals, we surmised that inelastic processes were important for the coupling of an external power supply to sustain the plasma. Let us examine some of these inelastic processes and their role in reactions occurring within discharges. The chemical identities of the gas phase species assume increased importance in determining the specific inelastic processes. The energetics of the inelastic processes depend to a great extent on the energy levels intrinsic to the gas species.

Five fundamental inelastic processes account for the majority of chemical processes occurring in plasmas: (a) ionization, (b) excitation, (c) relaxation, (d) dissociation, and (e) recombination. Many other processes that occur in discharges are species dependent. All five fundamental processes can be found in a plasma of hydrogen as the energy input to the plasma is gradually increased. To illustrate the fundamental inelastic processes, let us begin by following the plasma chemistry of hydrogen in a hypothetical situation where all electrons have equal energies and this energy can be gradually increased.[11]

At low energies, electron–H_2 collisions are elastic and the electrons suffer momentum changes only as shown in Figure 6.4. The H–H bond strength is approximately 4.5 eV so we would expect atomic hydrogen to form when the electron energies are increased to this level. However, the cross section for this process is small and the mechanism requires the hydrogen molecule

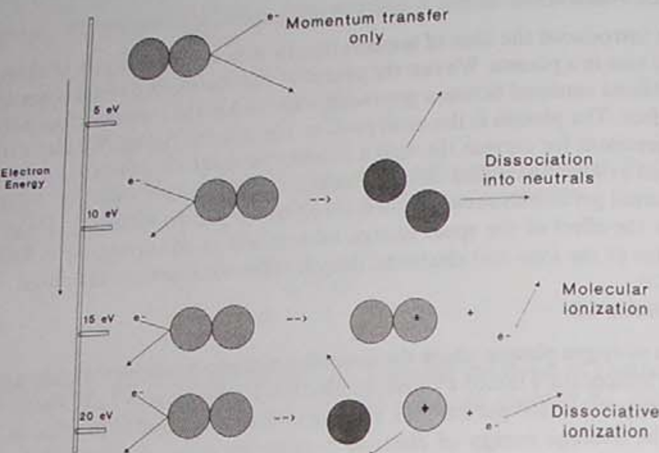


FIGURE 6.4. Plasma chemistry of the hydrogen molecule as the impinging electron energy is increased.

to be raised to a repulsive state. This excitation occurs at an energy of about 9 eV. Above this energy, electron impact results in the dissociation of the molecule to form two hydrogen atoms with each of them having significant kinetic energy. The ionization potential for H_2 molecules to form H_2^+ ions is 15.4 eV. At this energy, significant formation of singly ionized hydrogen molecules is seen. As the energy of the electrons is increased further, a repulsive state for the H_2^+ ion is reached, resulting in the formation of an H/H^+ pair. The hydrogen atoms produced have their own excited states, which can be achieved through collisions with lower-energy electrons. The excited states decay through collisions with other atoms, ions, or electrons.

In a typical glow discharge the electron energy distribution is Maxwellian, so all these processes can occur concurrently in the discharge. Bearing in mind this overview of the hydrogen molecule, let us consider each of the five processes in more detail.

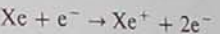
6.3.1. Ionization

Ionization in the plasma can occur through many mechanisms; the simplest is electron capture. For a neutral species having high electron affinity (as in

the case of halogens), the following reaction (shown here for fluorine) occurs readily:

$$F + e^- \rightarrow F^-$$

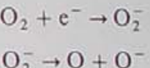
Electron capture contributes significantly to electron loss in halogen-containing plasmas.[12] An important mechanism for the maintenance of a glow discharge is the production of ions through electron impact. For instance, collision between an energetic electron and a xenon atom produces a xenon ion and another electron.



$$Xe + e^- \rightarrow Xe^+ + 2e^-$$

The two electrons are now accelerated by the potential gradient in a sheath to ionize more neutrals, starting a chain reaction. The electrons have to possess higher energy than the ionization potential of the neutral (~12 eV for xenon) for this process to occur.

For oxygen, the production of O^- ions occurs through a process known as resonance capture,[13] explained in the following sequence of reactions:



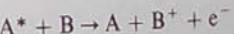
$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- \rightarrow O + O^-$$

The electron energy required for an ion to be produced is called its appearance potential, for oxygen it is 4.53 eV.

Photon emission from excited atoms can also lead to ionization.[14] Even though most of the photon energy in a discharge is dissipated as heat, energetic photons produce effects, such as Auger electrons, and can lead to significant ionization. Since the maximum photon energy can be as high as the direct potential difference between the electrodes, photoionization becomes important at high applied voltages.

Collisions between a neutral and a metastable species can produce ionization as well. This process, called the Penning ionization,[15] occurs as follows:

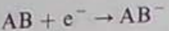


$$A^* + B \rightarrow A + B^+ + e^-$$

where the asterisk denotes an excited state. Similarly a collision between an ion and a neutral can result in a transfer of charge from the ion to the neutral.

Here is a typical ionization sequence of a molecular species in a plasma.

a. At low electron energies, resonance capture can give rise to a negative ion.

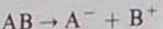


$$AB + e^- \rightarrow AB^-$$

b. This ion might dissociate.

$$AB^- \rightarrow A^- + B$$

c. At higher electron energies, the molecule can ionize during decomposition.



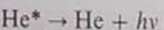
$$AB \rightarrow A^- + B^+$$

Notice the role of charged species collisions in producing unattached ionized species which would not otherwise be available for reaction. Reactions involving charged species would depend upon their concentration and their half-lives.

6.3.2. Excitation and Relaxation

Ionization is only an extreme case of the various excited states that an atom or a molecule can reach on electron impact. Figure 6.5 shows the ionization cross sections of different inert gas atoms. At energies smaller than the ionization potential, electrons with sufficient energy can raise a ground level species to one of the higher available states. Figure 6.6 shows the energy level diagram of a helium atom.[16] Notice the number of nonionized excited states available to the atom. Similar to ionization, there are electron energy thresholds equal to the energy of the first excited state, and they need to be exceeded for the excitation to occur.

Certain excited species are metastable (lifetimes longer than 1 ms), others have very short lives in the excited state (typically 100 ns or less). When the lifetime is short, excitation is frequently followed by relaxation processes such as radiative decay.



$$He^* \rightarrow He + h\nu$$

where $h\nu$ is the energy of a photon with frequency ν. As we saw earlier, this is the source of the glow associated with plasmas. Since the frequency of the emitted photon is specific to the species (corresponding to the energy difference between the excited state and the ground state), the emission

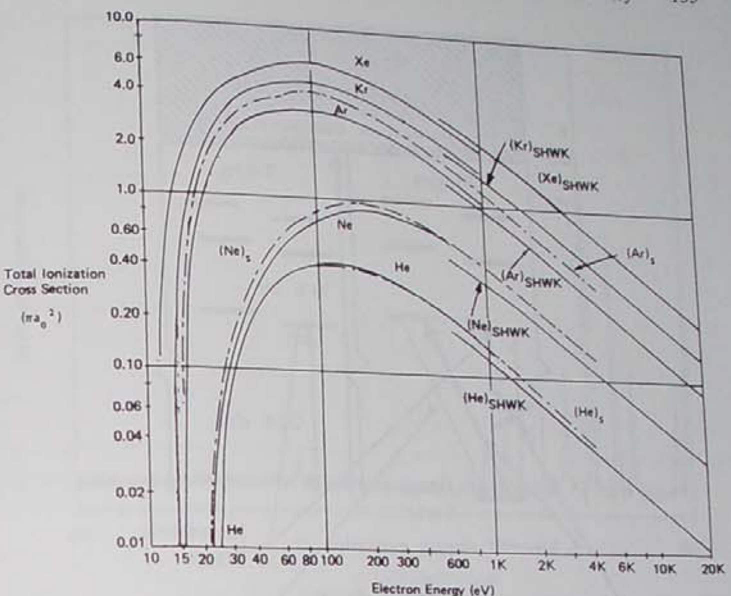


FIGURE 6.5. Ionization cross sections of different inert gases. Below a threshold energy the electrons produce little ionization. Ionization is only one of many excited states that an atom can achieve. Many curves for each gas are data from different sources. Reprinted from Ref. 3 with permission from John Wiley & Sons.

spectrum can be used in the plasma diagnostics. Optical emission spectroscopy of the plasma is often used to determine the etching endpoint in process plasmas. Figure 6.7 shows a discharge spectrum from an argon plasma. Notice the peaks corresponding to the various levels of the argon atom.

Metastable species, due to their longer lifetimes, can participate in other collisional processes, depending on their energy levels. These are called Penning processes, where collision between a metastable species and a neutral can result in the excitation or ionization of the neutral.

6.3.3. Dissociation

We have seen examples of dissociative ionization in earlier sections, when a molecule dissociates upon electron impact to either its constituent atoms or further ionized products. Of more relevance to CVD (and to etching processes in IC manufacture) is the formation of radicals in the plasma. Optical and

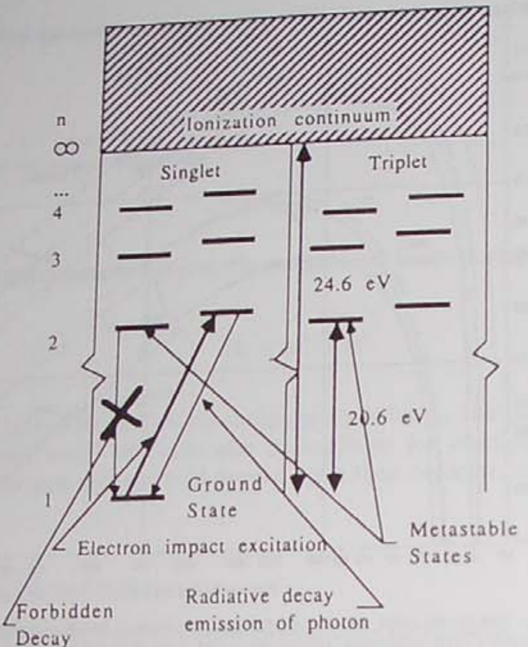
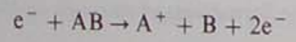


FIGURE 6.6. Energy level diagram of the helium atom. Notice the forbidden transitions. Understanding such energy diagrams is key to attributing the sources of the peaks in the glow discharge spectra. Reprinted from S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood (eds.), *Handbook of plasma processing technology*, p. 34, with permission of Noyes Publications © 1989.

mass spectroscopic evidence clearly indicates the presence of various radicals such as OH, NH_2, SiH_2, WF_x, etc., in a discharge.[17] The reaction of these radicals is often the path that leads to deposition in CVD and material removal during plasma etching. For instance, the formation of silicon from SiH_4 involves the formation of the intermediate SiH_2 radical. Formation of F and CF_x radicals in a CF_4 plasma are directly responsible for the etching of SiO_2.

Bond dissociation energies for the formation of these radicals are therefore important parameters when optimizing deposition processes. Bond dissociation energies can be calculated from the ionization potential for the radical and its appearance potential in the plasma. We can consider appearance potential to be a physical analog of heat of formation.



$$e^- + AB \rightarrow A^+ + B + 2e^-$$

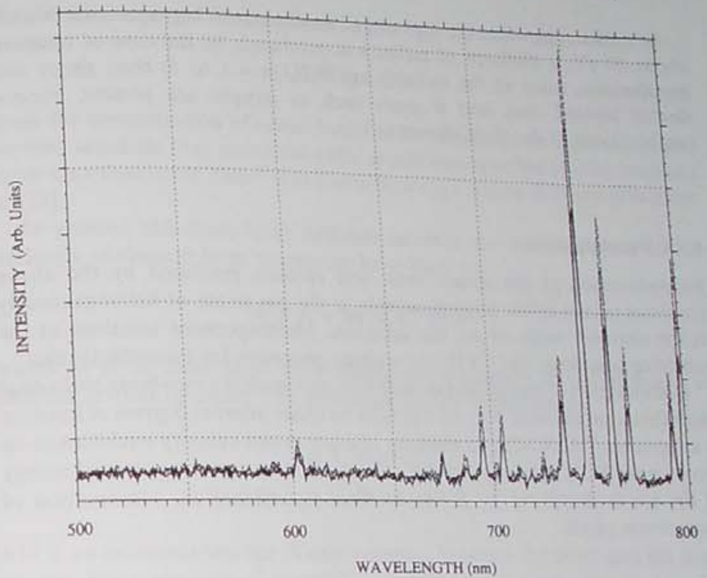
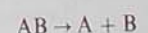


FIGURE 6.7. Glow discharge spectra can be used in qualitative and quantitative analysis of plasma reactions; this one is for argon.

and ionization potential to be equivalent to heat of reaction.

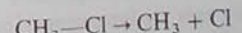
$$A \rightarrow A^+ + e^-$$

The sum of the two reactions



$$AB \rightarrow A + B$$

gives the bond energy for the formation of radical A from the compound molecule AB. Bond energies calculated by this method agree very well with those calculated by thermochemical methods. For instance, the bond dissociation energy for the following reaction



$$CH_3{-}Cl \rightarrow CH_3 + Cl$$

has been measured by electron impact to be 3.40 eV, and calculated from thermochemical data to be 3.47 eV.[18]

In a discharge, where the high end of the electron energy spectrum exceeds about 50 eV, a plethora of radicals is produced. In the case of tungsten hexafluoride, some of the radicals are WF_x ($x = 1$ to 5) their singly and doubly ionized ions, and if gases such as oxygen are present, various combinations of the three elements.

6.3.4. Recombination

Recombination of the atoms, ions, and radicals produced by the above processes occurs either homogeneously in the gas phase or heterogeneously at the chamber walls or on the substrate. Heterogeneous reactions at the substrate constitute the CVD and etching processes for microelectronics.

Conservation of energy and momentum implies that a two-body collisional recombination between two species with no other internal degrees of freedom is impossible.[19] Consider an electron of mass m and velocity v relative to an ion of mass M. If their combined final velocity is u and the potential energy of the ion is decreased by E due to their recombination, conservation of momentum yields

$$mv = (m + M)u \tag{6.25}$$

Conservation of energy yields

$$\tfrac{1}{2}mv^2 = \tfrac{1}{2}(m + M)u^2 - E \tag{6.26}$$

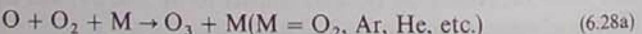
Solving for the final velocity u,

$$u^2 = -\frac{2Em}{(m + M)M} \tag{6.27}$$

However, since all the quantities on the right are positive, this yields an unreal solution for the final velocity.

Hence the only way a recombination process can occur is if there is a three-body collision (involving another ion, the wall or substrate, or a photon) or if there are other internal degrees of freedom to absorb or release energy.

The most common example of homogeneous recombination of atoms involving three-body collisions is the formation of ozone, which is commonly used in the CVD of SiO_2. The ozone-forming mechanism is as follows:



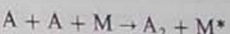
$$O + O_2 + M \rightarrow O_3 + M (M = O_2, Ar, He, etc.) \tag{6.28a}$$

The decomposition of ozone occurs as:

$$O + O_3 \rightarrow 2O_2 \tag{6.28b}$$

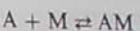
Since the concentration of ozone found in the discharges is relatively small, we may conclude that under the same conditions, reaction (6.28b) proceeds faster than reaction (6.28a).[20] The ozone-forming reaction (6.28a) is first-order in [O].

In general, the three-body collision reaction for the formation of the molecule of element from atoms can be written as

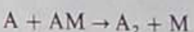


$$A + A + M \rightarrow A_2 + M^*$$

where M is an inert third body aiding the formation of the molecule of element A from its atom. The formation occurs in two stages.



$$A + M \rightleftarrows AM$$



$$A + AM \rightarrow A_2 + M$$

AM is an activated van der Waals' complex between the atom and the inert species. Since the rate of formation of AM is governed only by van der Waals forces between the two atoms, the rates of the reactions are fairly similar for most diatomic molecules.

Recombinations of ions by ion–ion collisions is much more probable than recombination by ion–electron collisions to form neutrals. This is due to the higher velocities of the electrons. Recombination rates for electron–ion processes are on the order of 1×10^{-9} per cm^3 per second. For ion–ion recombination, excess energy loss can be accommodated by the release of a photon, by both atoms reaching an excited state, or through three-body collisions. Three-body collisions involving the substrate are the most important processes at CVD pressures.[21]

Collisional recombination of radicals is extremely efficient. Since the large number of internal degrees of freedom of the radical allows redistribution of the energy, almost all collisions between radicals result in reactions such as disproportionation or combination.[22] The activation energy for these reactions is found to be close to zero, with rate constants as high as 10^{10} L mol^{-1} s^{-1}.

Exercise 6.3

An electron beam with an average energy of 50 eV, and a current density of 5×10^{-3} A/cm^3 is injected through a chamber containing CF_4 at a

pressure of 0.1 millitorr. If the cross section for impact ionization is
1×10^{-17} cm^2, what is the rate of ion production per centimeter of beam
path? The cross section of the electron beam is 1 cm^2.

6.4. PLASMA DIAGNOSTICS

Typical characteristics of the plasma, such as the presence of a glow discharge,
shielding of applied potential, or the presence of ionized atoms and molecules,
allow varied tools to be used in understanding the plasma. For instance,
increase in pressure of a closed cell containing a diatomic gas, upon striking
a plasma is an absolute measure of molecular dissociation.

Many intrusive and nonintrusive methods have been devised to measure
properties of plasmas. Techniques such as mass spectrometry have been
adapted to identify radicals in plasmas. Residual gas analysis of the
reaction chamber in CVD is intrinsic to the qualification of most processes
for manufacturing. An extensive overview is outside the realm of this book, but
we will look at three techniques unique to plasma enhanced chemical
processes. They are used to identify physical characteristics of the plasma,
such as electron density and temperature, and the nature and concentrations
of various chemical species.

6.4.1. The Langmuir Probe

The Langmuir probe uses the principles of Debye shielding and space
discharge limited current to directly determine the electron density and
electron temperature.[23] It is a conductive tip that can be placed anywhere
in the plasma, with suitable potentials applied to it as illustrated in Figure 6.8.

Let us examine the change in the probe current as the potential is changed
from negative to positive (Figure 6.8a). At very negative voltages, the probe
collects only ion current. At voltages close to zero on the probe, the probe
current is an exponential function of the applied voltage [$I_p \propto \exp(-V/kT_e)$].
When the voltage is made more positive, the current consists of randomly
arriving electrons ($J = ne\bar{v}/4$). By plotting the log of the probe current against
the applied voltage (Figure 6.8b), the slope of the line around the zero voltage
gives a measure of the electron temperature. The transition point to the lower
slope occurs at the plasma potential. The electron density can be found from
the current at the plasma potential.

Despite its simplicity, probe results can often be difficult to interpret,
especially in high frequency and electronegative discharges. High/low pass
filters need to be designed to eliminate noise. Several commercially available
probe packages contain appropriate software that automatically calculate

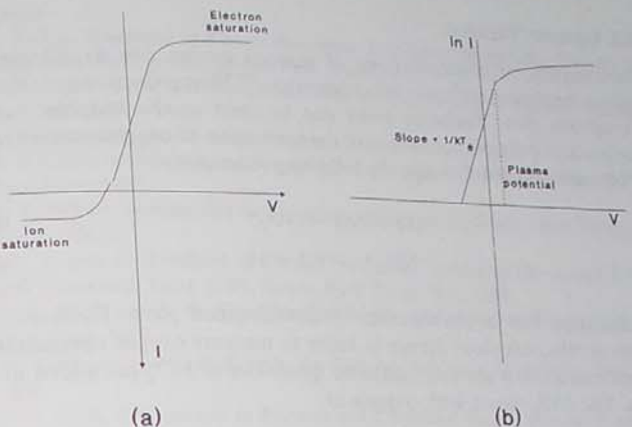


FIGURE 6.8. Voltage–current characteristics of a typical Langmuir probe. Note the ion and electron saturation currents and the calculation of plasma potential from this graph.

parameters such as plasma potential, Debye length, electron temperature,
and electron density.

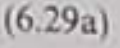
6.4.2. Optical Emission Spectroscopy

Recombination and/or decay of excited species results in characteristic
emission patterns. Since energies in discharges are high enough to produce
and excite species, optical emission spectroscopy can be used to identify the
presence of a species by analyzing the intensities of the optical spectrum at
different wavelengths.[24] However, quantitation of the concentration of species
is much more difficult, since the intensity at any wavelength is a function of
the species density and its electron impact excitation probability. However,
ratios of intensities at any given wavelength under different experimental
conditions can be used semiquantitatively as predictors of species concentration.

Detection systems for optical emission use many techniques for
discriminating between wavelengths, such as monochromators or a narrow-band filter and a photomultiplier tube. Identification of species is through
comparison of the spectrum to standard signatures of the species published
by NIST. Optical emission is widely used in etch systems to determine the
endpoint of a process.

6.4.3. Gaseous Titration

Determination of concentrations of gaseous species can be achieved by titrating the plasma with another reactive gas.[25] The production or extinction of a certain glow discharge color can be used as the endpoint for the titration. For example, quantitative determination of oxygen concentration can be accomplished through the following reactions:



$$O + NO \rightarrow NO_2^* \quad (6.29a)$$

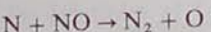
$$NO_2^* \rightarrow NO + h\nu \quad (6.29b)$$

The discharge has a characteristic yellowish-green glow. However, this reaction is relatively slow. Hence in order to measure oxygen concentration in a continuous flow system, measured quantities of NO_2 are added to the system. The NO_2 reacts with oxygen as

$$O + NO_2 \rightarrow O_2 + NO \quad (6.29c)$$

The NO in turn reacts with the oxygen to give the yellowish-green glow. When all the oxygen is consumed by reaction (6.29c) and none remains for reaction (6.29a), the glow is extinguished indicating the endpoint.

NO is also used for measuring active nitrogen concentration through the reaction



$$N + NO \rightarrow N_2 + O$$

Again the yellowish-green glow is used for endpointing.

6.5. SUMMARY

A review of the fundamental characteristics of plasmas was presented. We examined the relative concentrations of electrons, ions, and neutrals in the plasma, and studied their collective behaviour in modulating externally applied perturbations. We then examined the processes that occurred when these species collided with each other. The chemical nature of the atoms became important at this point, leading to the development of plasma chemistry. We studied the chemical reactions that occur in plasmas. Finally, we studied some plasma diagnostics to optimize the plasma for CVD applications.

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Chapter 7

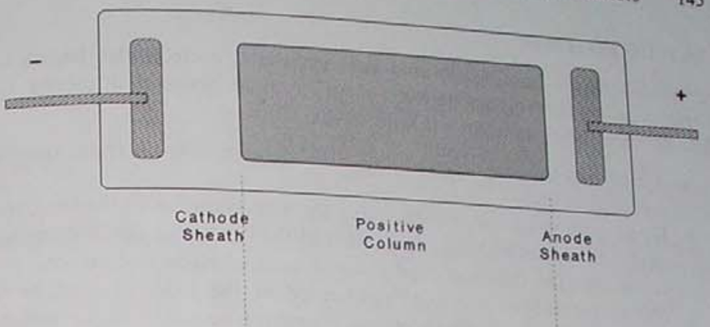
Processing Plasmas and Reactors

In our discussion of the fundamental characteristics of plasmas, we did not place emphasis on the means of generating and sustaining the plasma. Nor did we consider the proper confinement of the plasma and the reactants, or the optimization of the plasma in order to produce a solid film on the substrate. In this chapter we will address these issues and study the coupling of external power to the discharge for its generation and maintenance. We will use a simple DC diode plasma in order to illustrate electron production and loss mechanisms. However, since most useful CVD processes use AC power sources, we will also examine RF and microwave discharges.

Reactors for plasma CVD have several unique features compared with their thermal counterparts. We will consider different plasma reactor configurations and study two commercial plasma CVD reactors in detail.

7.1. DC BREAKDOWN AND DISCHARGE

The simplest (and historically the earliest means) of producing a laboratory plasma is by applying a DC voltage between two metal electrodes in an evacuated chamber containing an inert gas at low pressure. Figure 7.1a illustrates the apparatus required for such a setup. The details of the processes that occur when the voltage of the power supply is increased are covered by the references 1–3 at the end of this chapter. We will confine ourselves to two processes: the electrical breakdown of the gaseous column and the maintenance of the discharge after breakdown has occurred.



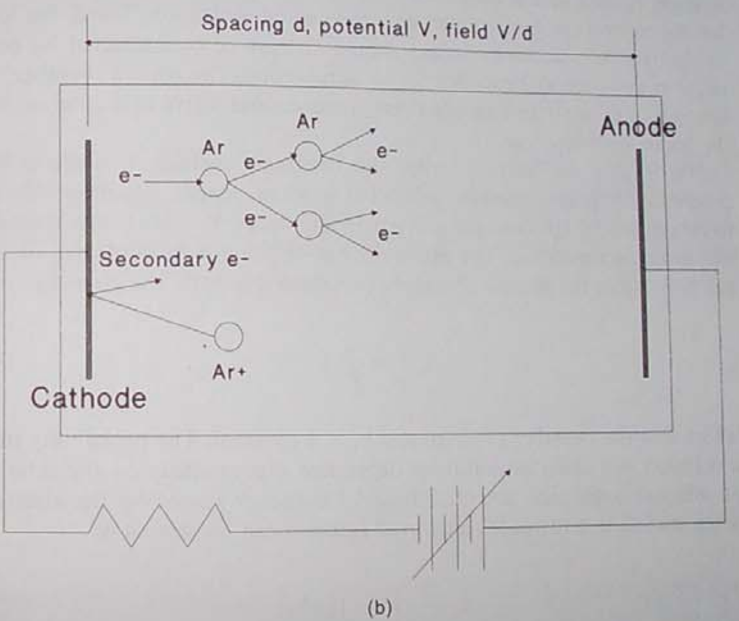


FIGURE 7.1. (a) A simple DC discharge column with a partially evacuated chamber and two electrodes. The potential distribution in a discharge is also shown. (b) Electron multiplication in a discharge column that leads to breakdown.

7.1.1. DC Breakdown

Qualitatively, the gaseous column between the two electrodes begins to conduct when the voltage between them is raised above a threshold V_B. The process occurs as follows (Figure 7.1b):

a. A stray electron near the cathode is accelerated towards the anode by the applied field.
b. Upon gaining sufficient energy, due to its acceleration in the field, the electron collides with a neutral atom in the discharge, causing impact ionization. The collision produces one more electron and an ion.
c. The two electrons are now accelerated in the field, causing more ionizations. The cascading processes of electron acceleration, ionization, and electron production results in the electrical breakdown of the gaseous column between the two electrodes.

In order for breakdown to occur, certain criteria have to be satisfied. First, the voltage between the two electrodes needs to exceed the critical breakdown voltage, V_B. Second, the distance d between the electrodes has to be sufficient for the electron to gain enough energy to cause ionization. Third, the loss of electrons by various processes should at least be counteracted by new electron production processes for a continuously increasing number of electrons. Let us try to quantify these processes and arrive at a criterion for the breakdown to occur.

We define a coefficient α (called the Townsend coefficient) which is the probability that an ionization will occur in a unit length. α is proportional to the number of collisions per unit length and the probability that a collision will cause an ionization. The probability of collision is proportional to the gas pressure in the plasma chamber. The mean free path λ is given by

$$\lambda = \frac{k_1}{P} \qquad (7.1)$$

where P is the chamber pressure and k_1 is a constant. The probability that a collision will cause ionization is dependent exponentially on the ratio of an effective ionization potential V_i and the energy gained by the electron when travelling a distance equal to λ. Hence α can be written as

$$\alpha = \frac{1}{\lambda}\exp(-V_i/eE\lambda) \qquad (7.2)$$

Let us consider now the total electron current reaching the anode. If the starting current from the cathode is I_c, the anode current rises from this

value exponentially with α, resulting in an anode current I_a given by

$$I_a = I_c e^{\alpha d} \qquad (7.3)$$

The same current due to ions will reach the cathode. However, when energetic ions impinge on the cathode, secondary electrons are emitted from the cathode with a probability of γ. The importance of the secondary electrons in maintaining the plasma will become evident shortly. However, for the present purpose of accounting for all the electrons, we can write the number of secondary electrons as

$$I_{se} = \gamma I_a(e^{\alpha d} - 1) \qquad (7.4)$$

where γ is the number of secondary electrons produced for every ion impact, also called the secondary electron yield. Hence the total current arriving at the anode will have successive I_{se}'s also being accelerated towards the anode, and I_a needs to be modified as

$$I_a = \frac{I_c e^{\alpha d}}{[1 - \gamma(e^{\alpha d} - 1)]} \approx \frac{I_c e^{\alpha d}}{[1 - \gamma e^{\alpha d}]} \qquad (7.5)$$

to account for the electrons produced by impact ionization in the gas phase and the secondary electrons produced by secondary emission at the cathode. When the denominator in equation (7.5) tends to zero, the current I_a tends to rise rapidly, resulting in breakdown. Noting that the breakdown voltage $V_B = E_B d$, we can combine this with equations (7.5) to arrive at

$$E_B = \frac{AP}{C + \ln(Pd)} \qquad (7.6)$$

and

$$V_B = \frac{APd}{C + \ln(Pd)} \qquad (7.7)$$

where A and C are constants that depend on the gas. Notice the electrode spacing and the gas pressure are intimately related in determining the breakdown conditions. At higher pressures, since the number of collisions is high, the distance between electrodes for breakdown can be small. Conversely, at lower pressures, the electrons travel longer distances before collision and

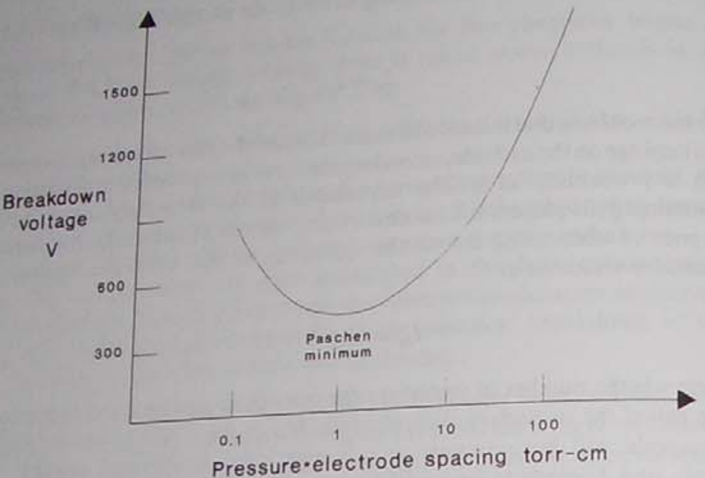


FIGURE 7.2. The Paschen curve for argon which illustrates the breakdown characteristics of the chamber as a function of pressure–electrode spacing product. The minimum in the curve is called the Paschen minimum.

a larger electrode spacing is needed for the same breakdown characteristics. Figure 7.2 plots the breakdown voltages for argon as a function of the product *Pd* of pressure and electrode spacing. The minimum in the breakdown curve is called the Paschen minimum.

7.1.2. Maintaining the DC Discharge

Once breakdown occurs, the various electron and energy loss mechanisms are simultaneously established: electron loss to the external circuit, recombination of electrons and ions at the walls, energy loss through heating of the electrodes and through optical emission, etc. To maintain the discharge at steady state, the production and loss of the species need to be balanced; energy from the external power supply needs to be coupled to the discharge to compensate for the energy lost. Before going into great detail, let us reiterate some of the fundamental characteristics of plasmas from Chapter 6.

a. The plasma is the most positive body in a discharge; it does not take a potential intermediate between the two electrode potentials.
b. The DC plasma is field-free; all fields are restricted to two sheaths, one surrounding each electrode.
c Each sheath field acts to repel electrons.

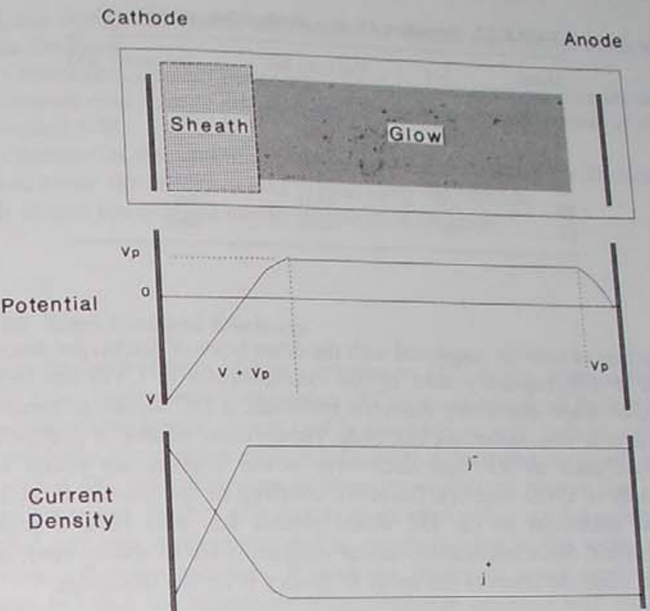


FIGURE 7.3. Potential and current density distributions in a DC discharge.

Using these ideas we can draw the potential curve of a CD discharge with a grounded anode and a cathode voltage of 1 000 V, as shown in Figure 7.3. Since there are no fields in the glow discharge itself, ion and electron accelerations occur in the sheaths only. And, most of the ionizations occur in the sheath and the sheath–bulk plasma transition, called the negative glow. This creates large gradients in current density in the sheath regions. A schematic of the ion and electron current density is also shown in Figure 7.3.

Even though ionization in the sheath and the glow produces electrons, the most important source of electrons, required for maintenance of the glow, is secondary electron emission from the electrodes and the chamber walls. Table 7.1 shows the secondary electron yield, γ, for various solid materials. Although secondary electrons can be produced from the bombardment of the solid by neutrals, electrons, and photons, the key mechanism is the ion current striking the cathode. Secondary electron production due to ion bombardment at low energies is an Auger neutralization process and is energy-independent up to several hundred electronvolts.

The DC diode plasma described so far is an inefficient process for the

TABLE 7.1 Secondary Electron Yields of Selected Materials

Metal	Ion	Yield per ion, γ	Ion energy (eV)
Si (100)	Ar	0.027	100
W	Ar	0.095	100
Al	Ar	0.12	slow
Al	N_2	0.10	slow
Ni	Ar	0.034	100
Fe	Ar	0.058	slow

production of radicals compared with the other types of discharges described below. It is infrequently used in this configuration in CVD reactors. In particular, when depositing dielectric materials, a DC discharge cannot be coupled to a nonconducting electrode. Hence other means of producing a discharge, such as RF and microwave power sources are found more commonly in CVD reactors. Inductive coupling of the plasma in place of the two electrodes in the DC diode plasma has also been a popular configuration. Since alternating current discharges are so widely used, let us examine what the effect of the input frequency is on the discharge.

7.2. FREQUENCY EFFECTS ON DISCHARGES

A DC discharge requires us to use conductive electrodes. Let us follow what happens if one of the electrodes, say the cathode, is made of an insulating material (this follows an explanation similar to Chapman[15]). If a DC voltage larger than the breakdown voltage is applied to the cathode, current flows until the insulator becomes charged up and terminates the discharge. If instead we apply a very low frequency AC voltage, during the first half of each cycle the insulator will charge up and extinguish the discharge. During the second half of each cycle, the insulator will discharge, and the current will flow in the opposite direction till the insulator charges up again. So the plasma essentially behaves like a capacitor, charging and discharging as the direction of the voltage changes. Since the capacitance C = charge Q/voltage V, and the charge Q = current $i \times$ time t, the typical charging time for a plasma using a quartz electrode is about 1 μs. So if the applied frequency does not allow sufficient time for the electrode to charge up and extinguish the discharge, i.e., it exceeds about 1 MHz, then a continuous discharge can be maintained. In reality, discharges can be maintained above about 100 kHz. Applied frequency above this level has some important effects on the discharge.

a. It can change the spatial distribution of species and electric fields in the discharge.
b. It determines whether the energy and the concentration of species are constant over time or whether they fluctuate over each period of the applied field.
c. It determines the minimum voltage required to maintain the discharge and hence the energy of ions bombarding the cathode.
d. It shapes the electron energy distribution function.

7.2.1. RF Breakdown and Discharge

Most commercial plasma reactors operate at 13.56 MHz, licensed by the Federal Communications Commission (FCC) as an industrial frequency at which commercial generators are readily available. At such high frequencies, the breakdown of a gaseous column between two electrodes is actually easier than with a DC field. Electrons undergo an oscillatory motion due to the applied frequency, so they gain energy more efficiently. And the oscillations minimize any loss mechanisms due to recombination at the walls, so the ionization efficiency increases. Breakdown occurs at lower peak-to-peak voltages. In effect, the impedance of the discharge decreases with increasing frequency, hence we can drive a higher current through the discharge for the same applied voltage. Secondary electrons, which are so important in maintaining the discharge in the DC case, are less important in the RF discharge. Furthermore, the efficiency of ionization in RF discharges is increased by phenomena such as the *surf riding effect*, where electrons gain energy by oscillating in and out of the sheath boundary.

At RF frequencies, the more massive ions have too much inertia to respond to the instantaneous electric field, unlike the electrons. This creates a time-averaged negative DC bias on one electrode, if that electrode is geometrically smaller than the other. This negative bias is often called self-bias, since it is not externally applied and develops due to electrode asymmetry. Such a configuration, where the effective area of one electrode is different from the other is called an asymmetric system. Asymmetric systems can be produced from electrodes with different geometrical areas or by confinement of the plasma. Confinement results in different *wetting* surface areas on the two electrodes; for instance, grounded walls effectively increase the total grounded electrode area. The self-bias is related to the effective area as

$$\frac{V_1}{V_2} = \left(\frac{A_2}{A_1}\right)^4 \tag{7.8}$$

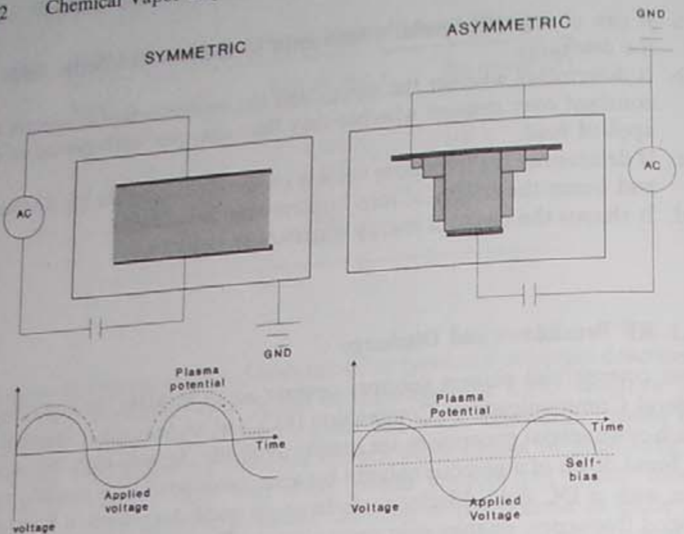


FIGURE 7.4. Symmetric and asymmetric discharges. Development of DC self-bias is also illustrated.

Either electrode may be grounded, but it is usually the larger electrode, including the chamber walls. The smaller electrode is often called the cathode. Since the plasma potential is the most positive body in the discharge, the potential follows the instantaneous fluctuations and the magnitude of the plasma potential is very small for the nonsymmetric system, as illustrated in Figure 7.4. This is important because the difference between the plasma potential and the negative DC bias on the cathode determines the energy of ions bombarding the cathode surface.

On a similar note, the DC bias developed in an asymmetric RF discharge is also inversely proportional to the gas pressure in the system. At high neutral densities, the discharge is able to put energy directly into the glow electrons and does not need as a high a sheath field to sustain itself.

Finally, notice the blocking capacitor and the matching network in Figure 7.5. In order to efficiently couple the RF energy to the plasma, an inductance/capacitance network is included between the plasma load and the generator.

RF generators are designed to have purely resistive internal impedance which as a standard is set to be 50 Ω. It can be shown that the maximum dissipation of power in a load occurs when the impedance of the load is the conjugate of the impedance of the generator. Since the generator is resistive

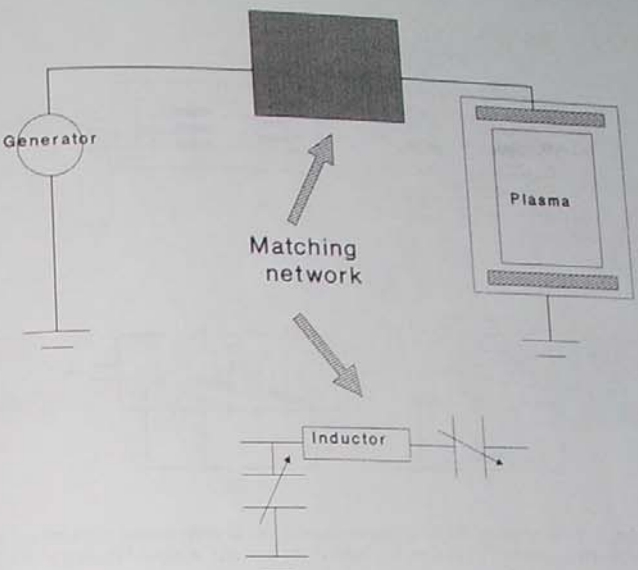


FIGURE 7.5. Matching network for an RF plasma. The capacitor/inductor network matches the plasma load to the generator output impedance of 50 ohms.

at 50 Ω, the changing impedance of the discharge needs to be tuned to this value by the matching circuitry. To get good power coupling, the matching circuitry often contains a fixed inductance coil and a variable capacitor whose value is adjusted with changes in the plasma. Obviously we would like to have zero power losses in the matching network, but that is seldom the case with most RF discharges.

7.2.2. Commercial RF Plasma Reactors

RF plasma CVD reactors have been in use since the mid-1970s for the deposition of dielectric films. Figure 7.6 shows four commonly used chamber and RF coupling configurations of PECVD reactors. In general, other than RF coupling, isolation of electrically hot surfaces, and proper grounding, gas flow and pressure control systems for PECVD reactors are similar to the LPCVD situation. Both single-wafer and batch type tools are available in the market, with sophisticated handlers and controlling software. Use of PECVD for the deposition of silicon nitrides, oxynitrides and oxides in

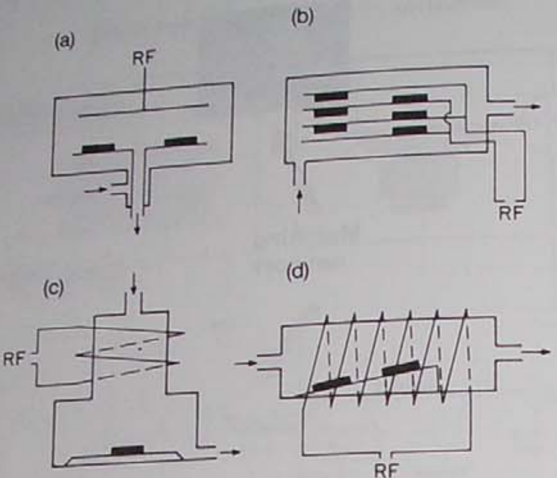


FIGURE 7.6. Four common RF coupling configurations in commercial reactors: (a) and (b) are capacitatively coupled; (c) and (d) are inductively coupled. Adapted from Ref. 9 with permission.

microelectronics is common. Amorphous and epitaxial silicon, metallic films including tungsten and TiN are in development.

Let us explore a typical commercial PECVD system made by Novellus Incorporated. The Novellus Concept One PECVD system is designed for the manufacture of SiN_x (using SiH_4, NH_3, and N_2), SiON (by adding N_2O), and low-SiH/UV-transparent nitride films along with doped and undoped SiO_2 (using SiH_4, N_2O or TEOS, O_2). Applications include passivation films, isolation films and spacer technology (see Chapter 9). It is a cold wall CVD system, capable of simultaneously applying two different frequencies to the substrate. Figure 7.7 shows the physical and electrical schematic of the reactor.

Wafers loaded by the cassette-to-cassette transfer arm, sequentially pass through multiple deposition stations before achieving their full deposition thickness. This helps in averaging the effects of the individual stations. Each of the deposition stations is a complete diode RF plasma reactor, with gas injection and wafer heating. The system uses no quartzware, and is also capable of plasma-based chamber cleans after a specified number of depositions. Both factors are instrumental in maintaining low particulate levels in the reactor. The wafers spend minimal time at elevated temperatures, resulting in reduced hillocking of the underlying aluminum metal. In the case of tetraethylorthosilicate (TEOS), a special liquid reactant delivery pump

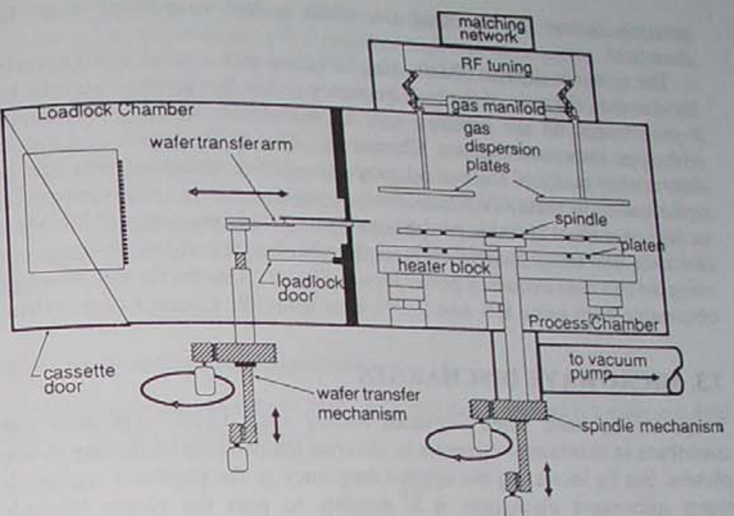


FIGURE 7.7. Schematic of the Novellus Concept One PECVD system with dual frequency for the deposition of dielectric films. Reprinted with permission from Novellus, Inc.

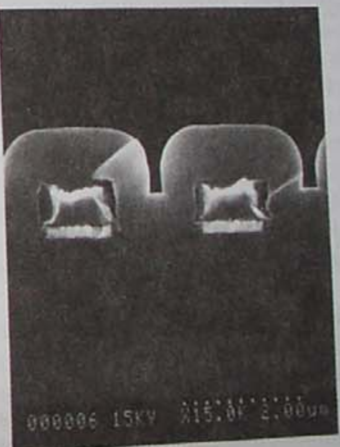


FIGURE 7.8. Film step coverage for a SiN film obtained with a Concept 1 system from Novellus. Reprinted with permission from Novellus, Inc.

precisely meters the incoming gas, which is flash evaporated inside the chamber.

The system is capable of delivering SiN films with a tunable SiH content. By changing the ratio of the high frequency to low frequency power, the ion bombardment on the substrate can be modulated, resulting in different hydrogen incorporation (see Chapter 9). The Si/H ratio is critical in determining many of the optical properties of the dielectric; films can be optimized to increase UV transparency, a requirement for passivation films in devices such as erasable programmable read-only memories (EPROMs). Similarly, film stress, controlled by ion bombardment, can also be optimized using the two dual frequency power inputs. Figure 7.8 shows the step coverage obtainable from using SiN and SiON films using the Concept One system.

7.3. MICROWAVE DISCHARGES

Frequency by itself, when increased further than 13.56 MHz does not contribute to substantial increases in electron temperature or density in the plasma. But by increasing the applied frequency to the gigahertz region, to create microwave discharges, it is possible to port the power through waveguides and resonance cavities such that there is no direct contact between the plasma and an electrode. It is also possible to use a magnetic field to interact with the electric field in order to produce high density plasmas. The ability to create a remote plasma without the presence of an electrode near the deposition region can be significant, since it allows the substrate to be separately powered, without influence from the plasma. Through proper

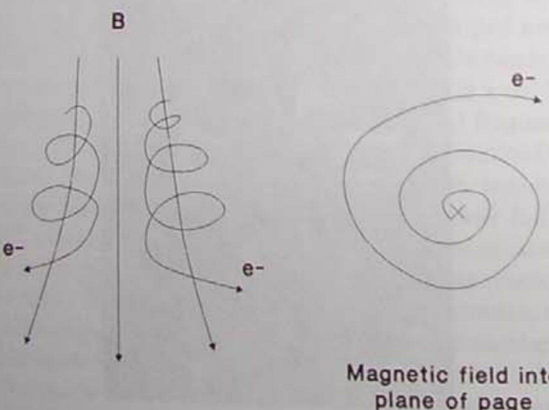


FIGURE 7.9. Electron trajectory in the presence of a magnetic field under resonance. The electron velocity and radius continuously increase.

choice of microwave coupling, microwave discharges can be maintained at pressures varying between a few millitorr and one atmosphere. Moreover, with the presence of an additional magnetic field to interact with the electric field, a variety of high density, low pressure plasmas can be created. Combining the two features, a high density plasma can be created using a microwave/ magnetic field configuration in a remote location, and active species can be extracted from the plasma to react on a substrate. This phenomenon is used in electron cyclotron resonance (ECR) plasma reactors to produce high step coverage, high deposition rate CVD processes, without causing radiation damage to the substrates, particularly for the growth of dielectrics.

7.3.1. Electron Cyclotron Resonance

In the presence of a magnetic field, electrons circle around the magnetic field lines with a frequency f where

$$f = \frac{qB}{2\pi m} \tag{7.9}$$

q is the electron charge and B is the magnet field in tesla (10^4 gauss). If an applied electric field with a frequency equal to the electron frequency is applied to the system, the electrons oscillate at resonance. Figure 7.9 illustrates the motion of an electron in a static magnetic field without a perpendicular electric field and when the condition for resonance is met. Notice the rapid rise in electron velocity due to the ECR heating of the electron.

Most ECR reactors operate at the S-band (2.45 GHz) so that moderate size magnets (875 gauss) can be used to achieve resonance. At the resonance condition transfer of electromagnetic energy to the discharge occurs simultaneously through elastic and inelastic collisions (Joule heating) and electron cyclotron heating of the electron gas. The electron gas then heats the neutral and ion species through elastic and inelastic collisions. Figure 7.10 schematically illustrates the energy transfer mechanisms in a differential volume in the reactor.

Reactor configurations vary according to the means by which the microwave energy is coupled to the reactor. In particular, waveguides and cavity applicators have become popular, their magnetic fields produced by coils or rare earth magnets. At the substrate end, often a separate RF bias is applied to extract ions and charged radicals from the microwave discharge. The substrate could have one of three configurations: (a) where the RF biased substrate is in the microwave discharge, (b) the substrate is separate but close

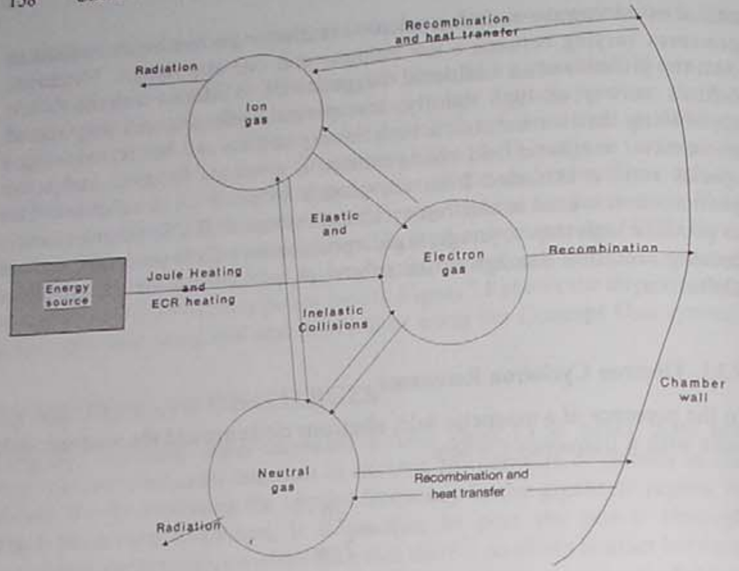


FIGURE 7.10. Energy transfer mechanisms in an ECR reactor. In the differential volume shown, ECR coupling to the electron transfers energy to the chamber. The other species are heated by collision with energetic electrons. Reprinted by permission, from Jes Asmussen, *J. Vac. Sci Technol. A.* 7(3), 883 (1989).

to the microwave discharge, or (c) the substrate is in a separate RF discharge, downstream from the microwave plasma. Each has advantages and disadvantages. In practice, the downstream plasma is more popular for commercial microelectronic CVD reactors as it protects the wafer from radiation damage that might be caused by the microwave discharge.

The main application of ECR reactors continues to be in plasma etching. However, commercial reactors for the CVD of SiO_2 and TiN are beginning to be available. We will study the configuration of the Lam EPIC ECR CVD reactor, used to deposit undoped SiO_2 for interlevel dielectric applications.

Figure 7.11 shows a schematic of the LAM EPIC reactor. 2.45 GHz microwave power is applied through a waveguide to the top of the plasma chamber. The ECR plasma chamber contains N_2O or O_2, and diluent gases such as argon. Silane for SiO_2 is introduced downstream in the wafer chamber to avoid unwanted silicon deposits. A separate 13.56 MHz RF power is applied to the substrate. This field along with the field shaping magnets

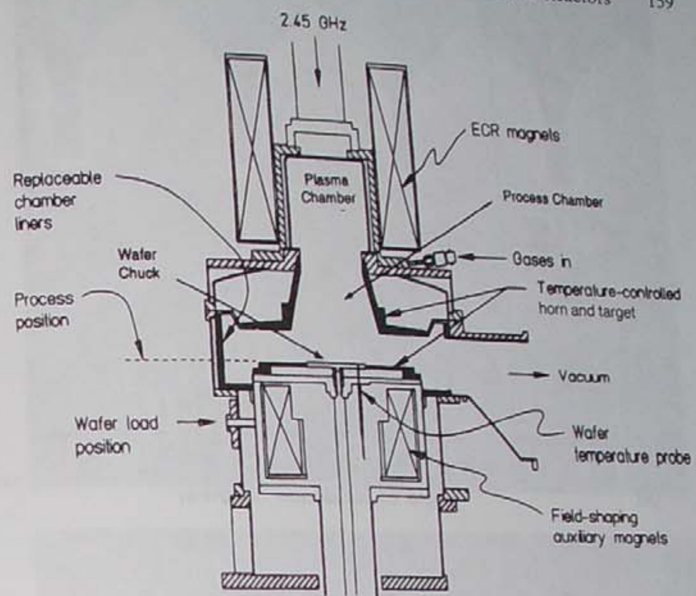
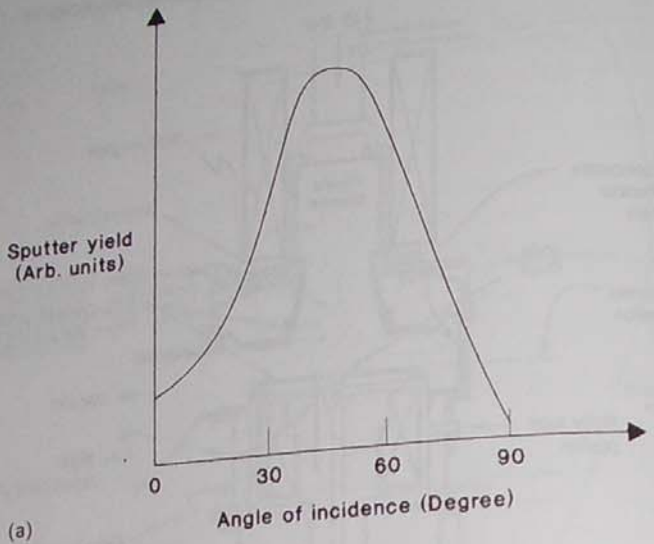


FIGURE 7.11. Lam Research Corporations EPIC ECR plasma CVD reactor. Reprint from the 1992 Proceedings of the VLSI Multilevel Interconnection Conference, p. 144.

below the substrate, help in extracting and directing the oxygen ions to the surface of the wafer, where they react with silane.

Higher RF bias on the substrate leads to higher energy ion bombardment and consequent sputter etching of the deposited film. Hence simultaneous etching and deposition processes occur, resulting in a characteristic film surface profile. Sputter etching produces enhanced etching on surfaces at 45° to the surface normal, so deposition results in increased step coverage with sharp cornered mesas, as shown in Figure 7.12. Figure 7.13 shows the surface profile as the etch/deposition ratio is varied through the bias. The higher the etch/deposition ratio, the better the step coverage. However, this results in reduced deposition rate and reduced throughput. The throughput needs to be optimized with the gap-filling requirement.

The diluent gas plays an important role in determining the sputter etch rate due to the mass of the etching ion. Hence care must be exercised in the choice of diluent gases. Film stress, silanol content, hence the refractive index and dielectric constant of the film, can also be modified by changing the O_2/SiH_4 ratio. In general better film properties are obtained at lower silane



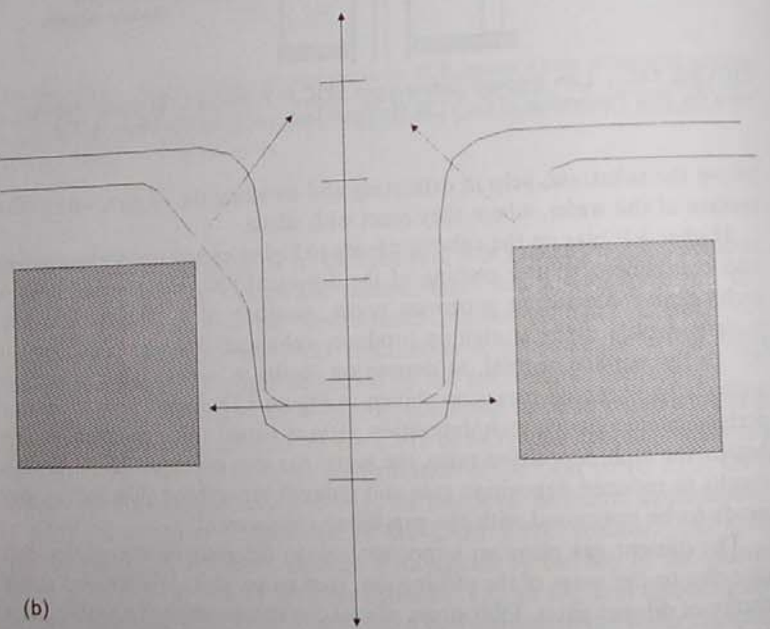
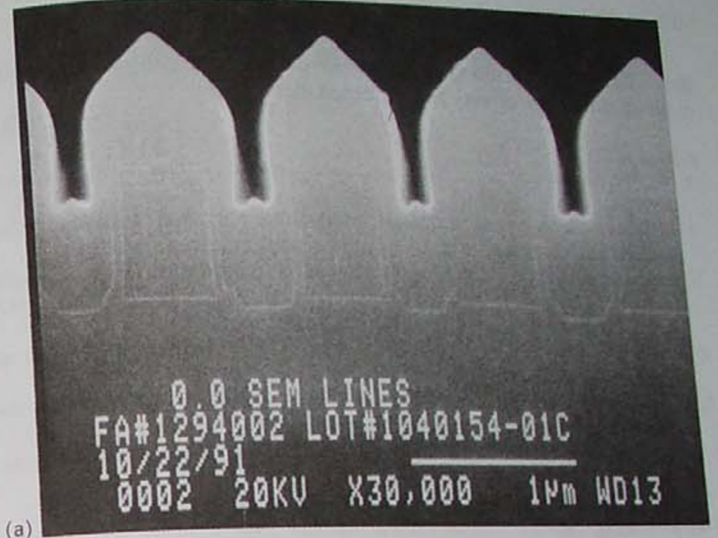


FIGURE 7.12. (a) Angular distribution of sputter etch rate. (b) The maximum at 45° leads to preferential etch and a consequent change in shape.



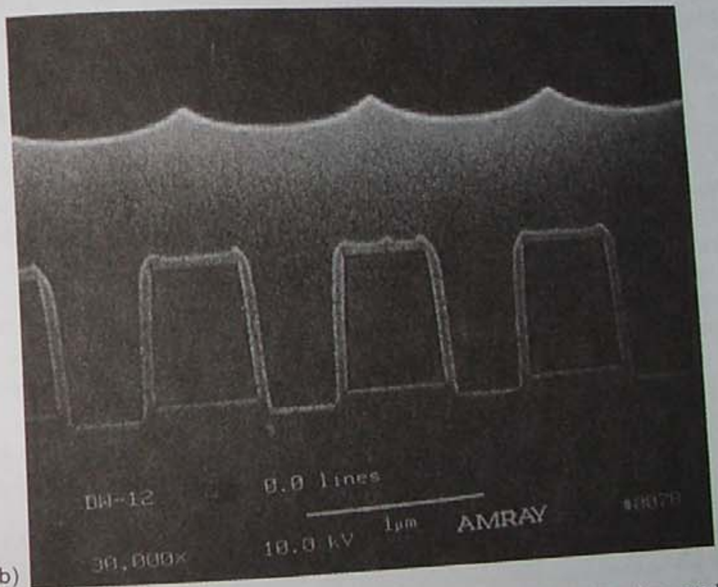


FIGURE 7.13. Surface profile as the etch/deposition ratio is changed. The sharp angular features in (a) are continuously smoothed to produce the more even surface in (b), which has a higher etch component. Reprint from the 1992 Proceedings of the VLSI Multilevel Interconnection Conference, p. 145.

flows. The ECR CVD interlevel dielectric is currently the only system capable of filling gaps between very finely pitched metal lines.

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Chapter 8

CVD of Conductors

Conductor systems in very large scale integrated VLSI circuits act as the conduits for signals to be transported to and away from electrical devices. As device dimensions and film thicknesses scale down, thin film properties of conductors (see Chapter 2) begin to dominate and special processing conditions become necessary. For instance, it becomes essential to lower the processing temperature so as to minimize undesirable thermally activated processes, such as hillock formation in aluminum-based metallization, or interdiffusion and reaction between adjacent films. Similarly, incorporation of impurities in the film matrix can result in significant degradation in properties, such as resistivity, film roughness, and stress, as the films get thinner. In this chapter, we will first review the requirements for conductor systems in VLSI circuits, without regard to the mode of deposition of the conductors. We will then consider the CVD of individual films, keeping in mind the device requirements. Finally we will examine more recent trends in CVD of conductors, with respect to new materials and with respect to newer CVD processes for established films.

8.1. GENERAL REQUIREMENTS FOR CONDUCTORS IN MICROELECTRONICS

Of all the properties of conducting films, electrical conductance is paramount in all interconnect applications. The choice of the material for the interconnect is based on the bulk value of the material's resistivity, and most of the work during the development of the deposition process is geared toward achieving a thin film resistivity close to the bulk value. The importance of electrical conductivity can be illustrated by the following analysis.[1]