3

Plasma Chemistry

3.1 INTRODUCTION

The initial interest and applications in cold plasmas chemistry were concentrated on synthesizing products in the plasma phase as a final result. Cold plasmas have been studied and used for synthesis of a variety of products in the gas phase, such as ammonia from hydrogen and nitrogen, oxidation of nitrogen, or formation of compounds of inert gases, such as XeF_4. A detailed list of examples can be found in Vursel and Polak [1]. The use of cold plasmas for surface activation of polymers was suggested already in 1968 by Beauchamp and Buttrill [2]. In the mid-1970's, when amorphous hydrogenated silicon was first deposited by PECVD, the direction of research and development started to shift toward the utilization of cold plasma chemistry for deposition of thin films and dry etching, with the microelectronics industry becoming the main user of both applications.

The main advantage of plasma assisted processing of solids evolves from the fact that the chemical reactions can take place at sample temperatures that are considerable lower than possible with thermal reactions taking place at thermodynamic equilibrium. It is, therefore, possible to deposit or grow films on substrates that do not have the thermal stability to accept such coating processes at higher temperatures. In addition, the lower treatment temperatures possible in the plasma are important when one has to limit diffusion or grain growth, especially in microelectronic processing where very small feature sizes and shallow junctions are involved.

In a plasma sustained in a gas at 0.1 to several torr, the electron temperatures reach tens of thousands of °K, while the temperatures of free atoms, molecules, or molecular fragments are only hundreds of °K. The chemical processes occurring in cold plasmas are driven by the energy of the discharge and are not based nor controlled by the temperature of the gas mixture or of the treated surfaces. The chemistry of the cold plasma is therefore a nonthermal, nonequilibrium process. Due to its nonequilibrium nature, the cold plasma has the unique property of efficiently generating chemically reactive species at low temperatures. The nonequilibrium steady-state conditions created by the high-energy electrons can transform a normally inert molecular gas such as carbon tetrafluoride (CF_4) into a highly reactive medium. All species of the cold plasma are essentially potential reactants.

The electrons, produced in the plasma by the partial ionization of the gas, act as the main agent for the transfer of energy from the external electric field to the gas. The energy transfer is done either by elastic or by inelastic collisions between the electrons and the molecules of the gas. Elastic electron-molecule collisions cause an increase in the kinetic energy of the molecules, while the energy transferred in inelastic collisions leads to dissociation and ionization of molecules and formation of plasma species such as free radicals, excited metastables, and ions.

Parallel to the generation of plasma species, a loss process also takes place in the plasma. Electrons are lost mainly by diffusion to the surfaces exposed to the plasma. Ions are similarly lost by diffusion and by recombination with electrons. Neutral atoms and radicals are lost primarily by recombination, through homogeneous reactions in the gas phase, or through surface reactions on the walls of the reactor.

Due to the large number and complexity of elementary reactions encountered in a plasma, it is not intended to give in this book a full account of all the possible reactions, their mechanisms, and kinetics. The differences between the characteristic times of various physical and chemical processes that take place in the cold plasmas are small and do not permit to distinguish between the diverse processes when considering chemical kinetics. In general, more than one reaction can contribute to the production and loss of each species adding to the overall complexity. In certain plasma systems, a single production or loss mechanism may be dominant. Detailed discussion of the reactions in the plasma are available in various monographs [3-5]. Only typical reactions will be presented and discussed in the next sections.

3.2 DEFINITIONS OF TERMS

The *probability of an interaction* between species in the gas phase is determined by the effective total cross section of the interactions. Since interactions in the plasma can be of many types, such as elastic collisions, ionization, charge transfer, dissociation, and so on, each type of interaction is characterized by a specific cross section.

For a given interaction between particles of type a and particles of type b, the mean free path between interactions, λ_{ab}, is defined as the average distance that a particle of type a will traverse through a group of particles of type b before undergoing a collision and is given by

$$\lambda_{ab} = \frac{1}{\sigma_{ab} n_b} \tag{3.1}$$

where σ_{ab} = cross section for the interaction
n_b = density of particles of type b

A particle a, moving at velocity v_a, will interact with a stationary group of particles of type b at a rate given by the collision frequency ν:

$$\nu_{ab} = \frac{v_a}{\lambda_{ab}} = v_a \sigma_{ab} n_b \tag{3.2}$$

If the density of particles a is n_a, the *rate of reaction*, R, will be

$$R = n_a \nu_{ab} = n_a n_b \sigma_{ab} v_a \, (\mathrm{cm}^3.\mathrm{sec})^{-1} \tag{3.3}$$

The neutral, chemically unstable fragments obtained by the dissociation of the molecules are called *radicals*. Neutral single atoms, fragments of multiatomic molecules, which are unstable and very active, can also be considered radicals and will be referred to as such. In this section, atoms will be marked as A, B; molecules as M; radicals as R; and excited species, at energetic levels above the ground level, with the superscript *, for example R^*. Atomic, molecular, or radical positive ions will be marked, respectively, A^+, M^+, and R^+.

Some species are excited to electronically energetic levels at which quantum mechanical selection rules forbid spontaneous transition to ground state. As a result such species have long lifetimes and are called *metastable species*.

For some gases (e.g., molecules containing halogen or oxygen atoms), it is thermodynamically advantageous for an electron to attach itself to an atom or molecule. This type of attachment is called *electron affinity* and the gases involved are *electronegative gases*.

3.3 CHEMICAL REACTIONS

The chemical reactions in a plasma reactor can be classified into homogeneous and heterogeneous reactions. The homogeneous reactions occur between species in the gaseous phase as the result of inelastic collisions between electrons and heavy species or collisions between heavy species. Heterogeneous reactions occur between the plasma species and the solid surfaces immersed or in contact with the plasma. In the description of homogeneous reactions we shall discuss separately reactions of electrons with heavy species and reactions between heavy species.

3.3.1 Homogeneous Reactions

3.3.1.1 Reactions of Electrons with Heavy Species

The electrons in the plasma gain energy from the external electromagnetic field and transfer it to the gas to excite and sustain the plasma. The major energy transfer from the electrons to the heavy species takes place by inelastic collisions. These inelastic collisions lead to a variety of reactions, the main ones being presented in the following.

Excitation. Impact of electrons of sufficient energy with heavy targets leads to the production of excited states of atoms and molecules, as described in the reactions:

$$e + A \rightarrow e + A^{*} \qquad (3.4)$$

$$e + A_2 \rightarrow A_2^{*} + e \qquad (3.5)$$

$$e + AB \rightarrow e + AB^{*} \qquad (3.6)$$

The *excitation* of the heavy species can be *vibrational, rotational,* or *electronic.* Atoms can only reach electronically excited states, while molecules can achieve rotationally and vibrationally excited states as well.

Electronically excited states return to ground state emitting their energy as electromagnetic radiation. This radiation accounts for the ultraviolet to visible emissions of the plasma. The relatively short lifetimes of excited species before radiative decay may preclude their participation in additional reactions. Metastable species are exceptions to this. Since metastables cannot return to their ground states by direct radiative transitions, they have long lifetimes and continue to participate in other reactions.

Dissociative Attachment. When electronegative gases are used, electrons of low energy (< 1 eV) can attach themselves to the molecules of the gas. If such attachment results in the formation of a repulsive electronically excited state, the molecule usually dissociates very fast ($\approx 10^{-13}$ sec), producing a negative ion according to equation

$$e + AB \rightarrow A + B^{-} \qquad (3.7)$$

Negative ions can also be produced by *dissociative ionization* reactions:

$$e + A_2 \rightarrow A^{+} + A^{-} + e \qquad (3.8a)$$

$$e + AB \rightarrow A^{+} + B^{-} + e \qquad (3.8b)$$

The reaction described by Eq. (3.7) is also called *dissociative capture*, while the reactions described by Eq. (3.8a) and Eq. (3.8b) are also called *ion-pair formation* reactions.

The threshold of the reaction described by Eq. (3.8b) is usually high compared to that of dissociative capture described by Eq. (3.7) because the formation of positive ions requires considerable energy. The maximum cross section is observed between 20 eV and 30 eV [6].

Some examples of dissociative attachment reaction are

$$e + O_2 \rightarrow 2O + e \rightarrow O + O^- \tag{3.9}$$

$$e + CF_4 \rightarrow CF_3 + F + e \rightarrow CF_3 + F^- \tag{3.10}$$

The reaction described in Eq. (3.9) is important in oxygen plasmas used for the stripping of photoresist in microelectronic processing. The reaction described in Eq. (3.10) is important in plasma etching of Si, SiO_2, and Si_3N_4. Atomic oxygen reacts easily with the organic materials used for photoresists to form volatile CO, CO_2, and H_2O, while atomic fluorine is the active species for etching silicon and silicon compounds in CF_4 discharges [7]. Halogens usually dissociate in a cold plasma according to Eq. (3.7) and Eq. (3.8b). For halides, which dissociate in cold plasmas according to Eq. (3.7) the electron energy required ranges from 1.88 eV for HF to 0.03 eV for HI [8].

The cross sections of the dissociative attachment reactions are dependent on the kinetic energy of the electrons and on the properties of the molecules involved. In certain cases the dependence of the cross section on the kinetic energy has the shape of a narrow resonance peak [6].

Typical values of cross sections for formation of negative ions by dissociative capture are given in Table 3-1 together with the energy of the impacting electron, W_{max}, at the maximum cross section. The examples of cross sections span a range from relatively high values of 10^{-14} cm^{-2}, at very low electron energies for I^{-1}, to very low values of 10^{-21} for H^-, at medium to high energies.

Dissociation. An inelastic collision of an electron with a molecule can cause its dissociation without the formation of ions, according to

$$e + A_2 \rightarrow 2A + e \tag{3.11}$$

$$e + AB \rightarrow e + A + B \tag{3.12}$$

TABLE 3-1 Cross Section for Dissociative Capture (adapted after [6], reprinted by permission of John Wiley & Sons, Inc.)

Molecule	Ion	W_{max} (eV)	σ (W_{max}) (10^{-17} cm^2)
HI	I^-	~0.0	2300
I_2	I^-	0.3	300
HBr	Br^-	0.28	27
HCl	Cl^-	0.81	1.99
O_2	O^-	6.7	0.143
CO_2	O^-	8.03	0.0482
H_2O	H^-	8.6	0.13
H_2	H^-	3.75	0.000016

The dissociation of molecules occurs only through their vibrational and electronic excitations. Most dissociation of molecules by slow electrons is induced by electronic excitation. The dissociation will occur only if the molecule is excited above a threshold value. For example, for H_2 the threshold value is 8.8 ± 0.2 eV and 9.6 ± 0.5 eV for formation of N atoms (see page 72 of [4]). The maximum cross section for electron impact dissociation of hydrogen molecules was observed at an electron energy of 16.5 eV, and its value is 9×10^{-17} cm^2 (see page 72 of [4]). A molecule in a vibrational excited state can be also further excited to dissociative states even by low-energy electron impact.

The cross section for vibrational energy excitation by electron impact can vary by two orders of magnitude from one molecule to another. Certain molecules, such as N_2, CO, and CO_2, have large cross sections of the order of $1\text{-}5 \times 10^{-16}$ cm^2, while others, such as H_2 and O_2 have cross sections that are smaller by a factor of 10–50 [9]. The dissociation of the excited molecule into neutral fragments occurs in a very short time of about 10^{-13} sec. Because the lifetime for radiative decay is longer than 10^{-7}–10^{-8} sec [4], the probability is almost 100% that the molecule will return to a lower energy state by dissociation and not by radiative decay.

Table 3-2 presents values of cross sections for the formation of neutrals and positive ions from the dissociation of CH_4 by collision with fast 100 eV electrons. The values for the formation of neutral radicals from CH_4 span the range of $0.1\text{–}2.4 \times 10^{-16}$ cm^2.

TABLE 3-2 Cross Sections for Formation of Neutral and Positively Charged Fragments from CH_4 (from [6], reprinted by permission of John Wiley & Sons, Inc.)

Positive Ions		Neutral Fragments	
Ion	σ ($\times 10^{16}$), cm^2	Species	σ ($\times 10^{16}$), cm^2
H^+	0.04	H	2.4
H_2^+	0.02	H_2	0.8
C^+	0.05	C	—
CH^+	0.14	CH	0.1
CH_2^+	0.28	CH_2	0.2
CH_3^+	1.5	CH_3	1.2
CH_4^+	1.8		—

The *dissociative attachment, dissociative ionization,* and *dissociation* reactions are a major source for the production of atoms, free radicals and negative ions in the cold plasma.

Ionization. Ionization in discharges taking place in a molecular gas occurs predominantly by electron impact that can produce positive or negative, atomic, or molecular ions:

$$e + A_2 \rightarrow A_2^+ + 2e \tag{3.13a}$$

$$e + A_2 \rightarrow A_2^- \tag{3.13b}$$

$$e + A_2 \rightarrow A^+ + A + 2e \tag{3.13c}$$

$$e + AB \rightarrow 2e + A^+ + B \tag{3.13d}$$

Ionization potentials of some atoms and molecules are shown in Table 3-3. As can be seen in the table, the ionization potentials span the range from 8 to 25 eV, which are well above the mean electron energy in a cold plasma. Thus, only electrons in the high-energy tail of the electron distribution can contribute to the ionization reactions. Ionization may sometimes occur also through a stepwise process, in which impact by lower-energy electrons cause first the excitation of the molecule to a metastable state. Subsequent impact of the metastable with an electron can cause its ionization. However, such a mechanism is not a dominant one.

TABLE 3-3 Ionization Potentials of Atoms and Molecules (in electron volts)

Neutral	Ion	Ionization Potential
Ar	Ar^+	15.8
Ar^+	Ar^{++}	27.6
F	F^+	17.4
H	H^+	13.6
He	He^+	24.6
N	N^+	14.5
O	O^+	13.6
Si	Si^+	8.1
CH_4	CH_4^+	13
C_2H_2	$C_2H_2^+$	11.4
H_2	H_2^+	15.4
HF	HF^+	17
H_2O	H_2O^+	12.6
N_2	N_2^+	15.6
O_2	O_2^+	12.2
SiH_4	SiH_4^+	12.2

The ionization reaction described in Eq. (3.13b) is also called a *resonance* or *nondissociative capture* reaction and can be followed by a dissociation, according to Eq. (3.7), as illustrated for oxygen:

$$e + O_2 \rightarrow O_2^- \rightarrow O + O^- \tag{3.14}$$

The threshold potential for this reaction is 4.53 eV, as compared to 17.28 eV for the direct formation of the $O^+ + O^-$ pair [8].

The reaction described in Eq. (3.13d) can produce a large number of different ions, when molecules containing a large number of atoms, such as higher hydrocarbons, are involved. An especially large number of ions is obtained from benzene, ranging from $C_6H_6^+$ to H^+ and covering the whole range $C_xH_y^+$ with $0 \leq x,\ y \leq 6$ [4].

Values of cross sections for the formation of different ionized fragments of CH_4 are shown in Table 3-2. The values span a two orders of magnitude range from 0.04 to 1.8×10^{-16} cm^2.

The dependence of the cross section of ionization for several molecules in the ground state on the electron energy is illustrated in Fig. 3-1.

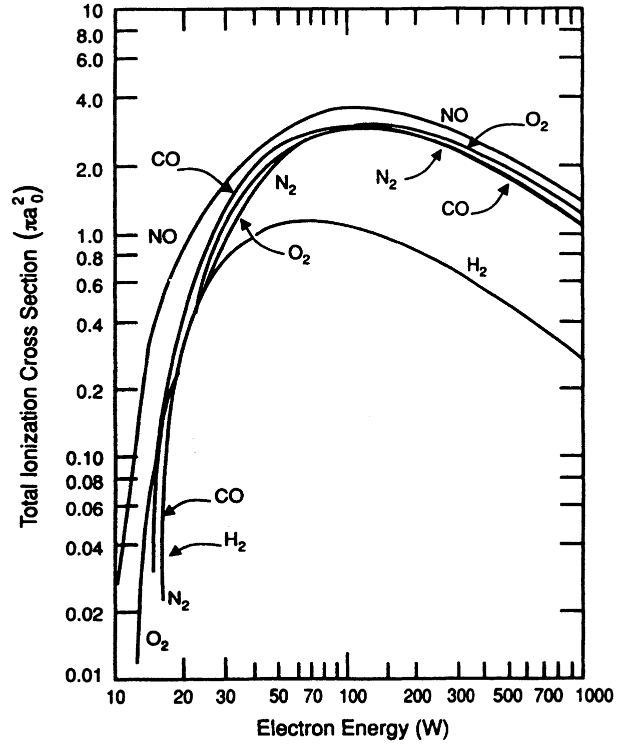

Fig. 3-1 Plot of cross section for ionization versus electron energy (from [6], reprinted by permission of John Wiley & Sons, Inc.).

Positive ions are usually formed in most ionization processes prevalent in the cold plasmas. Nevertheless, when the atom or molecule involved in the reaction possess electron affinity, negative ions can also form in the cold plasmas, according to Eqs. (3.7), (3.8a), and (3.13b). The process described by Eq. (3.13b) is a radiative attachment that is very slow and its typical cross section is 10^{-19} cm^2 at a few electron volts [10].

Oxygen, halogens, and halogen-containing molecules are some of the molecules with a tendency to form negative ions. For these molecules the cross sections have high values at low electron energies, as illustrated in Table 3-1. In addition to direct ionization, or dissociative attachment described earlier, negative ions can also form through radiative or nondissociative electron capture (e.g., I^-, Br^-).

Recombination. The charged particles (electrons and ions) are lost from the plasma by recombination of particles of opposite charges. Recombinations that take place between electrons and atomic ions are accompanied by emission of electromagnetic radiation and are called *radiative recombinations*:

$$e + \mathrm{Ar}^+ \rightarrow \mathrm{Ar} + h\nu \tag{3.15}$$

where h = Planck's constant
ν = radiation frequency

The term $h\nu$ indicates release of radiation energy.

On the other hand, the release of energy during the recombinations of electrons with molecular ions can cause the dissociation of the molecule by a *dissociative recombination* reaction:

$$AB^+ + e \Leftrightarrow AB^* \rightarrow A^* + B \tag{3.16a}$$

$$e + A_2^+ \rightarrow 2A \tag{3.16b}$$

The rates of recombination of electrons with atomic ions, Eq. (3.15), are very low, in the range of 10^{-13} $cm^3.sec^{-1}$. The rates of recombination with molecular ions, Eqs. (3.16a) and (3.16b), are much higher, in the range 10^{-9} to 10^{-10} $cm^3.sec^{-1}$ [8].

3.3.1.2 Reactions Between Heavy Species

Reactions between heavy species are those occurring during collisions of molecules, atoms, radicals, and ions. The reactions between the heavy species can be grouped in two subcategories, namely, *ion-molecule* and *radical-molecule reactions*. Ion-molecule reactions are those that involve at least one ion. Radical-molecule reactions are the reactions occurring between neutral species only.

The density of molecules in a gas at a pressure of 1 torr is $\sim 3.5 \times 10^{16}$ cm^{-3}. In a plasma with a mean electron energy of 1 eV, sustained in a gas characterized by a molecular dissociation energy of about 5 eV and an ionization energy of 10 eV, the density of dissociated molecules can be estimated to be 10^{14} cm^{-3} [11]. The density of ions and electrons in a cold plasma is usually about 10^9 to 10^{11} cm^{-3}. Thus, in a cold plasma, the three densities are related by

$$n_i \ll n_r \ll n_n \tag{3.17}$$

where n_r is the radical density.

Because of these relative particle densities, it can be expected that the radical-molecule reactions will be generally more important than will ion-molecule reactions in plasma chemistry. This is indeed the case in many processes. However, ion-molecule reactions can have significant contributions to plasma chemistry and can enhance the rate of the total reaction occurring in the plasma

[12]. Following is a description of the more important types of plasma reactions in each subcategory.

Ion-Molecule Reactions

Recombination of ions. Two colliding ions can recombine to form a molecule in the ground state and release their energy trough emission of radiation:

$$A^+ + B^- \rightarrow AB + h\nu \tag{3.18}$$

A collision between two ions can also result in the *neutralization* of the ions by formation of two excited atoms:

$$A^+ + B^- \rightarrow A^* + B^* + h\nu \tag{3.19}$$

Because the total energy of the recombining ions is generally larger then the total energy of the excited neutrals the surplus energy is released through radiation.

Ion-ion recombination can also take place trough a three-body collision:

$$M + A^+ + B^- \rightarrow AB + M \tag{3.19a}$$

The two-body reaction described by Eq. (3.18) is important at very low pressures, while three-body recombination occurs at pressures above 0.1 mtorr.

Charge transfer. An electric charge may be transferred during a collision between an ion and a neutral particle. The transfer can take place between identical partners, for example,

$$A + A^+ \rightarrow A^+ + A \tag{3.20}$$

or dissimilar partners:

$$B_2 + A^+ \rightarrow B_2^+ + A \tag{3.21a}$$

$$A^+ + BC \rightarrow A + BC^+ \tag{3.21b}$$

Although it appears from Eq. (3.20) that this reaction has no effect, it results in fact in a slower ion and a faster neutral. The symmetric processes described by Eq. (3.20) are characterized by large cross sections. At low energies, the asymmetric processes involving molecules — (described by Eq. (3.21)) — are frequently characterized by large cross sections, whereas the ones involving atoms are characterized by small cross sections. Charge transfer can occur in reactions with either positive ions as just described or with negative ions.

When the charge transfer takes place with dissociation of the colliding species, according to Eq. (3.22), the reaction is called *charge transfer with dissociation*:

$$A^+ + BC \rightarrow A + B^+ + C \tag{3.22}$$

The reaction rate constants of ion-molecule charge transfer reactions are typically of order of 10^{-10}–10^{-12} cm^3.sec^{-1} [13].

Transfer of heavy reactants. This type of ion-molecule reaction results in the formation of new compound species as in Eq. (3.23):

$$A^+ + BC \rightarrow \begin{cases} AB^+ + C \\ AB + C^+ \end{cases} \tag{3.23}$$

The reaction is sometimes also called *ionization by interchange*. Examples of such transfer reactions are:

$$N^+ + O_2 \rightarrow NO^+ + O \tag{3.24}$$

$$N + O_2^+ \rightarrow NO^+ + O \tag{3.25}$$

These reactions of heavy reactant transfer occur with rate coefficients greater than 10^{-9} cm^3.sec^{-1}. Detailed discussions of ion-molecule reactions can be found in [14].

Associative detachment. In a collision between a negative ion and a radical, the ion can attach itself to the radical, neutralizes by releasing the electron, and forms a new compound. This is an *associative detachment* reaction described by the equation

$$A^- + BC \rightarrow ABC + e \tag{3.26}$$

Radical-Molecule Reactions

Radical-molecule reactions are those where only neutral species act as reactants. The active radicals may be either multiatom radicals or single atoms, fragments of multiatomic molecules. The radicals are unstable and chemically very active. Representative radical-molecule reactions are presented in the following.

Electron transfer. This is a reaction between two neutral particles resulting in the formation of two ions by the transfer of an electron between the colliding neutrals:

$$A + B \rightarrow A^+ + B^- \tag{3.27}$$

This type of reaction requires that at least one molecule has very high kinetic energy and its occurrence in cold plasmas is therefore rare.

Ionization. A collision between two energetic neutrals can cause the ionization of one of them:

$$A + B \rightarrow A^+ + B + e \tag{3.28}$$

Penning ionization/dissociation. The Penning reactions occur during collisions involving energetic metastable species. In the collisions of metastables (B^*) with neutral species, the excited metastables transfer their excess energy to the target, causing ionization or dissociation according to Eq. (3.29a) or Eq. (3.29b):

$$B^* + A \rightarrow A^+ + B + e \tag{3.29a}$$

$$B^* + A_2 \rightarrow 2A + B \tag{3.29b}$$

The Penning processes are particularly important in plasmas sustained in mixtures, which include gases such as argon and helium, that are characterized by several long-lifetime metastable states. Furthermore, Penning ionization has a large cross section, which enhances the probability of this process.

For Penning reactions to take place, the energy of the metastable species must be higher than the ionization or dissociation potential of the other species participating in the reaction. Metastable energies are in the range of 0–20 eV (11.5 eV for Ar, 16.6 eV for Ne). As illustrated in Fig. 3-2 for nitrogen, for certain gases at lower electron energies, the cross sections for metastable excitation are much higher than the cross sections for ionization. In such conditions, electron impact causes formation of a larger number of metastable particles than ions. The metastable species can accumulate energy and reach energy levels higher than the ionization threshold of the interacting species, and this can release their energy by Penning ionization. Penning dissociation is a similar process that results in the dissociation of the target molecule into neutral radicals instead of its ionization.

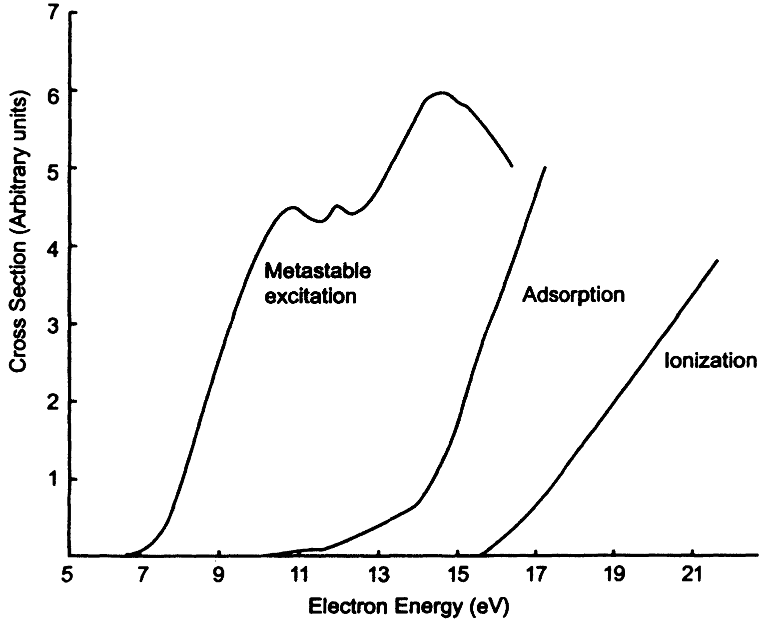

Fig. 3-2 Cross sections versus electron energy for metastable excitation and ionization of nitrogen (from [15], reprinted with permission from H. F. Winters, *Topics in Current Chemistry, Plasma Chemistry III*, ed. S. Veprek and M. Venugopalan, Berlin: Springer-Verlag, 1980).

During collisions of metastable atoms with certain molecules (for example, H_2O, NH_3, SF_6), the metastable atom can release its energy by becoming itself ionized according to the reaction:

$$B^{*} + M \rightarrow B^{+} + M + e \tag{3.30}$$

When the molecule involved in the reaction is SF_6, a negative ion is formed through the attachment of the released electron to the SF_6 molecule:

$$B^{*} + SF_6 \rightarrow B^{+} + SF_6^{-} \tag{3.31}$$

The cross section for the last reaction is $(1.7 \pm 0.11) \times 10^{-12}$ cm^2.

Attachment of atoms. These are reactions similar to the associative detachment reactions of the ion-molecule type described by Eq. (3.26) but involve only neutral species:

$$A + BC + M \rightarrow ABC + M \tag{3.32}$$

Disproportionation. The disproportionation reaction ressembles to the ion-molecule transfer of heavy reactants reaction, but it occurs between neutral species according to

$$A + BC \rightarrow AB + C \tag{3.33}$$

Recombination of radicals. Collisions between the chemically active radicals can cause their recombination into stable molecules. The requirement of simultaneous conservation of both the energy and momentum prevents the direct recombination of two monoatomic radicals. Recombination of monoatomic radicals can therefore take place only through a multibody collision, when the third body might be another particle in the plasma or a solid surface in contact with the plasma. The large number of degree of freedom of multiatomic free radicals allows the redistribution of internal energy, and the conservation of momentum and energy can be achieved in a two-body recombination. Therefore, the collisional efficiency of recombination for multiatomic radicals becomes close to unity.

Radicals usually combine through two type of reactions:

- *Disproportionation*

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6 \tag{3.34}$$

- *Combination*

$$2C_2H_5 \rightarrow C_4H_{10} \tag{3.35}$$

Chemiluminescence. Excitation of an atom or a molecule can take place in the plasma during a collision with another atom. The excitation can occur during a chemical reaction (e.g., disproportionation or recombination), but can also take place without the occurrence of a chemical reaction. The two possibilities are illustrated by Eq. (3.36) and Eq. (3.37):

$$A^{*} + BC \rightarrow A + BC^{*} \tag{3.36}$$

$$B + CA \rightarrow BC^{*} + A \tag{3.37}$$

Equation (3.36) describes a Penning-type reaction. The excited radical BC^{*} usually returns from its excited state to its energetic ground level by radiative decays:

$$AB^{*} \rightarrow AB + h\nu \tag{3.38}$$

Equations (3.36)–(3.38) describe the chemiluminescence reactions that can occur in the plasma and contribute to its luminescence [16].

3.3.1.3 Comments on Homogeneous Reactions

At pressures of about 1 torr, the free radical concentration in a cold plasma is up to 10^5 higher than the ion concentration. Therefore radical-molecule reactions usually occur at faster rates than do ion-molecule reactions. It was found experimentally that addition of radical forming halogen compounds to hydrocarbon monomers accelerates significantly the polymerization rate and reduces the hydrogen to carbon ratio in the polymer [17]. However, in certain conditions, superposition of ion-molecule reactions can strongly accelerate the overall reaction kinetics. An example of such a behavior was observed in the deposition of silicon from plasmas of silicon tetrachloride ($SiCl_4$), hydrogen, and argon.

In plasmas of $SiCl_4 + H_2$ the dissociation of $SiCl_4$ and deposition of Si occur through radical-molecule reaction [12]. In plasmas of $SiCl_4$ + Ar the reactions occur through ion-molecule processes and the overall reaction rates are much smaller than in the $SiCl_4 + H_2$ plasma. However, the superposition of ion-molecule reactions on radical-molecule reactions in plasmas of $SiCl_4 + H_2$ + Ar causes a strong enhancement in the overall reaction rate and the Si deposition rate. In this case the enhancing effect of the Ar was explained by an increase in the H radical concentration, through interactions of Ar^+ and metastable Ar^* with hydrogen molecules [12].

The homogeneous chemical reactions occur predominantly in the cathode fall and positive column regions of the glow discharge. The highest rate of reaction is observed in the cathode fall, where the strength of the electric field is highest (see Fig. 2-4 in Sec. 2.1.2). However, in situations where the cathode fall occupies only a small fraction of the total reaction volume, the overall reaction rate can be significantly affected also by the positive column.

The occurrence of a specific reaction is obviously a function of the gases involved and is determined by the minimal energy required for that reaction. If the plasma species involved have enough energy for the reaction to occur, the reaction and its rate are also determined by the cross section of the reaction.

The cross section is also a function of the energy of the species, as already indicated in Fig. 3-1 and Fig. 3-2. The cross sections and reaction rate constants for the various reactions cover a wide range of values, even for a plasma sustained in a simple molecular gas. This is illustrated in Table 3-4 for an oxygen plasma.

As can be seen in Table 3-4, the values of the cross sections for reactions occurring in an oxygen plasma span a range of values from 10^{-20} to 10^{-16} cm^2. Even for the same type of reaction, the cross sections can vary up to two orders of magnitude from one molecule to another. Typical cross sections for various types of reactions just described can be found in [4, 5, 10, and 18].

A characteristic situation encountered in cold plasmas is illustrated in Fig. 3-3, which shows the cross sections for electron-impact ionization of argon together with the Druyvesteyn energy distribution of the electrons in an argon plasma, at a typical electron temperature $T_e = 5$ eV. As illustrated in Fig. 3-3, the majority of the electrons in this plasma have energies that are either smaller than the threshold for ionization or correspond to very low ionization cross sections.

TABLE 3-4 Cross Sections and Reaction Rate Constants in an Oxygen Plasma (from [5], reprinted by permission of John Wiley & Sons, Inc.)

Reaction	k	σ_{max} (cm^2)
Ionization		
1. $e + O_2 \rightarrow O_2^+ + 2e$		2.72×10^{-16}
2. $e + O \rightarrow O^+ + 2e$		1.54×10^{-18}
Dissociative ionization		
3. $e + O_2 \rightarrow O^+ + O$		1.0×10^{-16}
Dissociative attachment		
4. $e + O_2 \rightarrow O^- + O$		1.41×10^{-18}
5. $e + O_2 \rightarrow O^- + O + e$		4.85×10^{-19}
Dissociation		
6. $e + O_2 \rightarrow 2\,O + e$		2.25×10^{-18}
Metastable formation		
7. $e + O_2 \rightarrow O_2(^1\Delta_g) + e$		3.0×10^{-20}
Charge transfer		
8. $O^+ + O_2 \rightarrow O_2^+ + O$	2×10^{-11} cm^3/sec	
9. $O_2^+ + O \rightarrow O + O_2$		8×10^{-16}
10. $O_2^+ + O_2 \rightarrow O_3^+ + O$		1×10^{-16}
11. $O_2^+ + 2\,O_2 \rightarrow O_4^+ + O_2$	2.8×10^{-30} cm^6/sec	
12. $O^- + O_2 \rightarrow O_2^- + O$	2.5×10^{-14} cm^3/sec at $E/p = 20$ V/cm torr 3.4×10^{-12} cm^3/sec at $E/p = 45$ V/cm torr	
13. $O^- + O_3 \rightarrow O_3^- + O$	5.3×10^{-10} cm^3/sec	
14. $O^- + 2\,O_2 \rightarrow O_3^- + O_2$	$1.0 \pm 0.2 \times 10^{-30}$ cm^6/sec	
15. $O_2^- + O \rightarrow O^- + O_2$	5×10^{-10} cm^3/sec	
16. $O_2^- + O_2 \rightarrow O_3^- + O$		$< 10^{-18}$
17. $O_2^- + O_3 \rightarrow O_3^- + O_2$	4.0×10^{-10} cm^3/sec	
18. $O_2^- + 2\,O_2 \rightarrow O_4^- + O_2$	3×10^{-31} cm^6/sec	
19. $O_3^- + O_2 \rightarrow O_2^- + O_3$		4×10^{-17}
20. $O_4^- + O \rightarrow O_3^- + O_2$	4×10^{-10} cm^3/sec	
21. $O_4^- + O_2 \rightarrow O_2^- + 2\,O_2$	6×10^{-15} cm^3/sec	
Detachment		
22. $O^- + O \rightarrow O_2 + e$	3.0×10^{-10} cm^3/sec	
23. $O^- + O_2 \rightarrow O + O_2 + e$		7×10^{-16}
24. $O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$	~ 3×10^{-10} cm^3/sec	
25. $O_2^- + O \rightarrow O_3 + e$	5.0×10^{-10} cm^3/sec	
26. $O_2^- + O_2 \rightarrow 2\,O_2 + e$		7×10^{-16}
27. $O_2^- + O_2(^1\Delta_g) \rightarrow 2\,O_2 + e$	~ 2×10^{-10} cm^3/sec	
Electron-ion recombination		
28. $e + \left\{\begin{matrix} O \\ O_2^+ \\ O_3^+ \\ O_4^+ \end{matrix}\right\} \rightarrow \left\{\begin{matrix} O \\ 2\,O \\ O + O_2 \\ 2\,O_2 \end{matrix}\right\}$	$\lesssim 10^{-7}$ cm^3/sec	

TABLE 3-4 *cont.* Cross Sections and Reaction Rate Constants in an Oxygen Plasma (from [5], reprinted by permission of John Wiley & Sons, Inc.)

Reaction	k	$\sigma_{\max}$ (cm^2)
Ion-ion recombination		
29. $\left\{\begin{matrix} O^- \\ O_2^- \\ O_3^- \\ O_4^- \end{matrix}\right\} + \left\{\begin{matrix} O^+ \\ O_2^+ \\ O_3^+ \\ O_4^+ \end{matrix}\right\} \rightarrow \left\{\begin{matrix} O \\ O_2 \end{matrix}\right\}$	$\sim 10^{-7}$ cm^3/sec	
Atom recombination		
30. $2\,O + O_2 \rightarrow 2\,O_2$	2.3×10^{-33} cm^6/sec	
31. $3\,O \rightarrow O + O_2$	1.5×10^{-34} cm^6/sec	
32. $O + 2\,O_2 \rightarrow O_2 + O_2$	$1.9 \times 10^{-35} \exp(2100/RT)$cm^6/sec	
33. $O + O_3 \rightarrow 2\,O_2$	$2.0 \times 10^{-11} \exp(-4790/RT)$cm^3/sec	
34. $O \overset{\text{wall}}{\rightarrow} O_2$	$\gamma = 1.6 \times 10^{-4}$ to 1.4×10^{-2} ($T = 20 - 600$ °C)	

As a result, only the small fraction of electrons that have energies in the high energy tail of the distribution curve will cause the ionization of the gas.

In most ionization processes prevalent in cold plasmas, positive ions are formed. However, when the atom or molecule involved in the reaction possess electron affinity, negative ions can also form according to Eqs. (3.8a), (3.7), and (3.13b). Electron attachment to neutral atoms happens most easily to those atoms that have almost filled outer electron shells, for example, oxygen, halogens, or halogen-containing molecules. The source of the electron can be another atom, molecule, or a free electron.

The negative ions formed by the nondissociative capture of electrons by complex molecules according to Eq. (3.13b) are long-lived negative ions. The long lifetimes of such ions are due to the fast distribution of the electronic energy over vibrational degrees of freedom, thus making difficult the reverse transition necessary for detachment of electrons. The coefficient for attachment of electrons to SF_6 molecules by this mechanism was found to be 1.24×10^9 cm^{-1}.torr^{-1}, and the lifetime of an excited SF_6^- ion was estimated as 25 μs [19].

The formation of negative ions causes the replacement of highly mobile electrons with much slower heavier ions. Large densities of negative ions will change the ambipolar electron diffusion coefficient and thereby the fluxes of electrons and positive ions. This results in the reduction of the electrical conductivity of the plasma that may cause plasma instabilities. Such instabilities, in turn, can impede the control of the process and make it difficult to achieve uniformity of results.

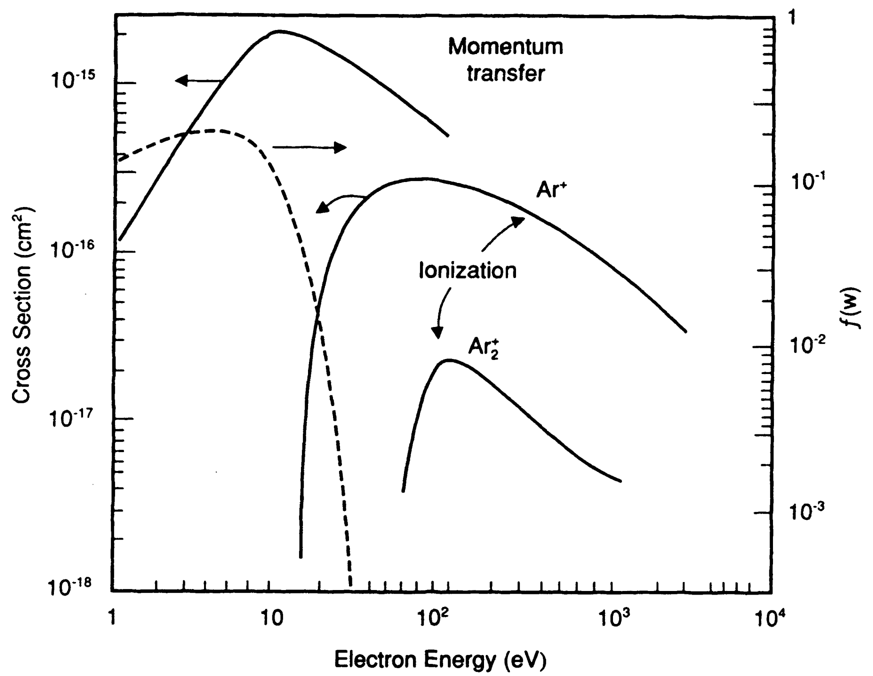

Fig. 3-3 Cross sections versus electron energy (—) and Druyvesteyn energy distribution for $T_e = 5$ eV (- -).

3.3.2 Heterogeneous Reactions

The heterogeneous reactions are those which occur as a result of interactions between a solid surface (S) exposed to the plasma and plasma species. The plasma species can be an individual atom (A, B), a monomer molecule (M), a simple radical (R), or a polymer (P) formed in the plasma. Typical heterogeneous reactions are presented next.

Adsorption. When molecules, monomers, or radicals from the plasma come in contact with a surface exposed to the plasma they can be adsorbed on the surface. The adsorption reaction can be described by

$$M_g + S \rightarrow M_s \tag{3.39a}$$

$$R_g + S \rightarrow R_s \tag{3.39b}$$

The indexes g and s indicate, respectively, a specie in the gas or solid phase. Most radicals interact with surfaces, and consequently the composition of the deposited film will be largely determined by the relative fluxes of all film-forming species [20].

Recombination or compound formation. Atoms or radicals from the plasma can react with species already adsorbed on the surface to combine and form compounds according to

$$S - A + A \rightarrow S + A_2 \tag{3.40a}$$

$$S - R + R_1 \rightarrow S + M \tag{3.40b}$$

$S - A$ indicates an atom A adsorbed on the surface S.

During recombination, the energy of the particles participating in the reaction is usually released as heat to the surface. The rate of surface recombination is strongly dependent on the catalytic properties of the surface [21]. For example, the probability of recombination of fluorine atoms ($F + F \rightarrow F_2$) on Teflon is small (7×10^{-5}) [22], while on copper it is approximately three orders of magnitude higher [23]. Surfaces that are good catalysts for recombinations can be passivated by the addition of small amounts of impurities to the gas.

Metastable deexcitation. An excited metastable specie M^* from the plasma can release its energy and return to the ground state by collision with a solid surface. The reaction

$$S + M^* \rightarrow S + M \tag{3.41}$$

describes the metastable deexcitation reaction.

Sputtering. A surface exposed to the plasma is always negative relative to the plasma causing positive ions from the plasma to accelerate toward the surface. If an ion A^+ arrives at the surface with sufficient energy, it can remove an atom from the surface:

$$S - B + A^+ \rightarrow S^+ + B + A \tag{3.42}$$

This process is called sputtering. The atom B in Eq. (3.42) can be in this case either an atom from the solid surface or an atom adsorbed on it. The sputtered neutral atom enters the plasma with a kinetic energy of several electron volts.

Almost 95% of the sputtered atoms originate within a few angstroms of the surface as a result of a collision cascade within the solid.

Polymerization. Radicals in the plasma can react with radicals adsorbed on the surfaces and form polymers:

$$R_g + R_s \rightarrow P_s \tag{3.43a}$$

$$M_g + R_s \rightarrow P'_s \tag{3.43b}$$

Polymerization or radical formation can also happen between two species adsorbed on the solid surface:

$$R_s + R'_s \rightarrow P_s \tag{3.44a}$$

$$M_s + R_s \rightarrow R'_s \tag{3.44b}$$

3.3.2.1 General Remarks

The recombination reactions described by Eq. (3.40a) and Eq. (3.40b) can cause either the deposition of a solid film or etching of the surface if the formed compound is volatile. The polymerization reactions, Eq. (3.43a) to Eq. (3.44a), also result in a deposition of a film.

In metastable deexcitation, Eq. (3.41), or in recombination, Eq. (3.40b), reaction atoms on the surface act as a third body.

When a molecular ion collides with a solid surface, it is generally dissociated into its constituent atoms. Upon collision, part of the kinetic energy of the ion is transferred into internal energy, which is generally much larger than the energy required to break the chemical bond. This causes the dissociation of the molecular ion on impact on the solid surface. For example, the energy required to break the bond between the atoms of the nitrogen molecule is about 9 eV. It was found that the probability of breaking up an N_2^+ ion on collision with a solid surface has a threshold of around 9 eV and reaches 100% at ~ 100 eV, as shown in Fig. 3-4 [15].

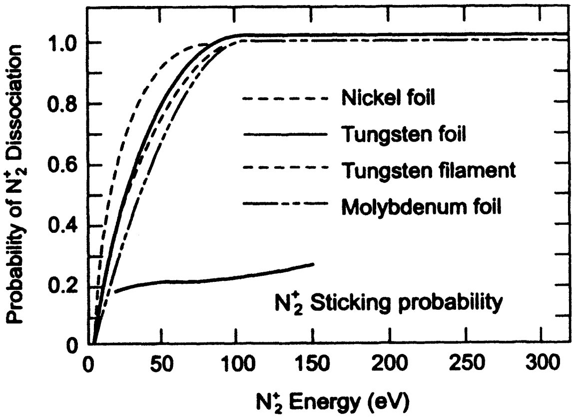

Fig. 3-4 Probability that an N_2^+ will dissociate upon collision with a surface versus ion energy (from [15], reprinted with permission from S. Veprek and M. Venugopalan, eds., *Topics in Current Chemistry, Plasma Chemistry III*, Berlin: Springer-Verlag, 1980).

These energies correspond to the substrate biases or self-biases encountered in a DC- or RF-excited plasma. Some of the atoms or radicals produced by the dissociation of molecular ions are reflected from the surface, while others are incorporated into its crystal lattice. The reflected atoms are likely to react with the surrounding surfaces or may be incorporated in the growing film. It was found, for example, that there is a 20% probability that the nitrogen atoms resulting from the dissociation of the N_2^+ ion will stick to the surface and eventually form a thin nitride layer of 20–30 Å. The other 80% of the nitrogen atoms are reflected into the gas phase. Similarly, bombardment of a surface with O_2^+, or CH_4^+ will cause formation of a surface layer of oxide or carbide.

Negative ions are usually ignored in the mechanistic discussions of plasma processing of surfaces. Because any surface in contact with a plasma is at a negative potential relative to the plasma, the negative ions created in the plasma cannot reach the surfaces and are usually ignored in the discussion of plasma interaction with surfaces. However, in some situations negative ions will participate in surface reactions. Such situations arise whenever a negatively biased surface has a tendency to form negative secondary ions when bombarded with positive ions. These negative ions will be accelerated into the plasma by the sheath potential, and if the operating pressure and interelectode distance are sufficiently low, the negative ions can traverse the plasma arriving at the opposite electrode with substantial kinetic energy. This effect has been observed during sputter deposition of halides and plasma deposition of high-temperature superconducting materials [20].

3.4 THE CHEMICAL REACTION CHAIN

The chemical processes in the plasma follow several steps: *initiation, propagation, termination*, and *reinitiation* [12, 17].

In the initiation stage free radicals or atoms are produced by collision of energetic electrons or ions with molecules. The radical formation takes place by dissociation of molecules in the gaseous phase or of molecules adsorbed on the surface of the substrate or on the deposited film. Both molecules and radicals are adsorbed on the surfaces exposed to the plasma.

The propagation step of the reactions can also take place in both the gas phase and on the modified surface (deposited film, etched surface). In the gas phase, propagation involves the interaction between radicals, ions, and molecules in ion-molecule and radical-molecule reactions. Propagation takes place on the solid surface through interactions of surface free radicals with either gas phase or adsorbed molecules, radicals, or ions.

In the termination step, reactions similar to those described for propagation result in the formation of the final product.

Reinitiation develops when radicals, which are formed through conversion of the deposited film or dissociation of polymers, again enter the reaction chain. The conversion to radicals can be caused by impact of energetic particles or by photon absorption.

The complexity of the reaction chain is illustrated in Fig. 3-5 for PECVD deposition of amorphous silicon from Ar + H_2 + $SiCl_4$ plasmas [24]. The initiation, propagation, and termination steps are shown with the various types of reactions taking place in each step.

During PECVD deposition processing it is important to prevent the termination of the main reaction chain in the homogeneous gas phase or the occurrence of homogeneous reactions that can result in formation of solid powders. If not prevented, these homogeneous reactions will affect the film deposition rate and the quality of the deposited films. They can also cause contamination, whose prevention is becoming extremely and increasingly important in the microelectronics industry.

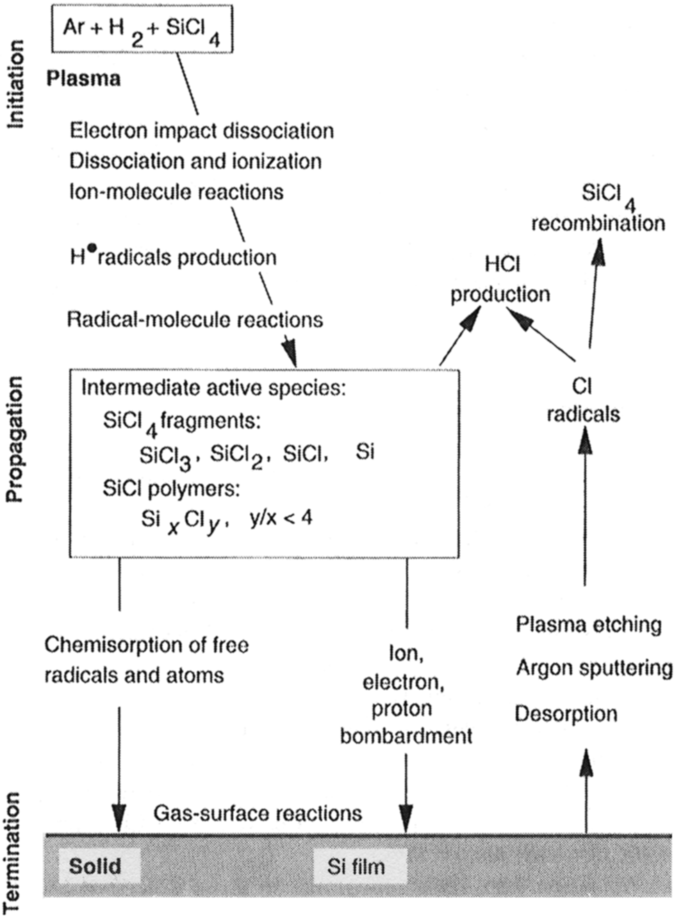

Fig. 3-5 The reaction chain during deposition of silicon from Ar + H_2 + $SiCl_4$.

A schematic summary of the different types of reactions that can take place in a cold plasma reactor is presented in Fig. 3-6. Reactions under plasma conditions can cause formation of plasma species and final products that cannot otherwise be obtained by reactions under thermodynamic equilibrium. For example, species such as N_x with $x > 2$ [25], for nitrogen-containing plasmas, and Si_xCl_y with $x \geq 2$ [26], for plasmas containing silicon tetrachloride, have been observed only in cold plasmas. Special polymers have also been obtained by plasma polymerization (see Sec. 7.1).

Due to the multitude of the phenomena affecting the plasma and the resulting complexity of the plasma chemistry, it is not always possible to control the pathways of the chemical reactions or to predict from first principles the right combination of process parameters required for a certain outcome of the process. The kinetics of chemical reactions in a cold plasma can be considered as a

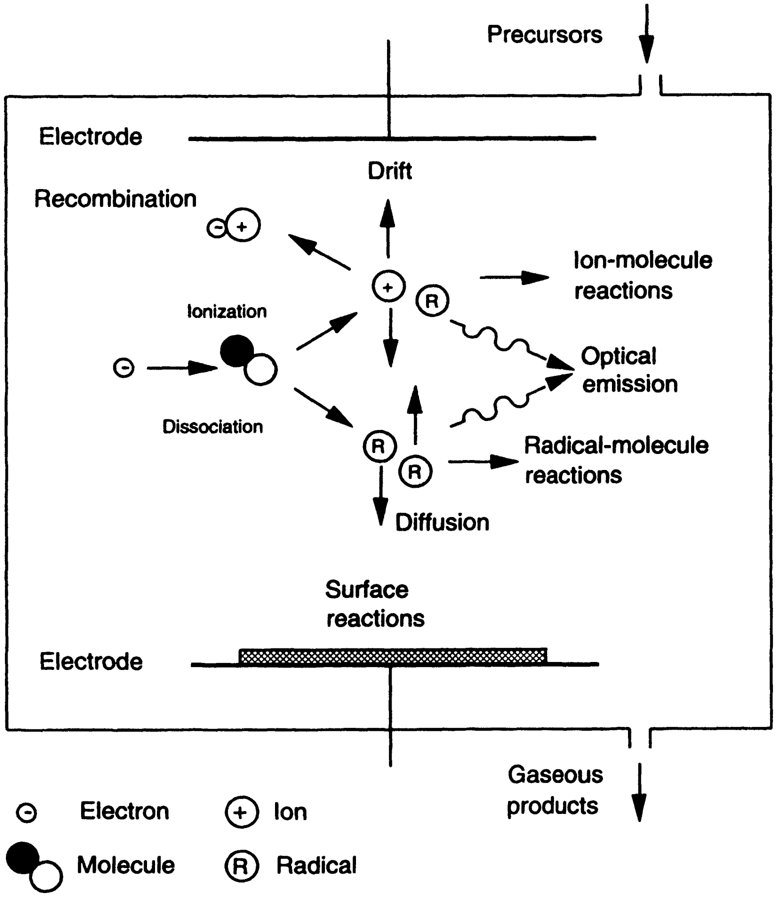

Fig. 3-6 Schematic diagram of reactions in a plasma reactor.

particular case of non-equilibrium chemical kinetics. While equilibrium kinetics can be explained by means of theories of elastic collisions, the kinetics of plasma chemistry also has to take into account inelastic collisions. In the absence of thermodynamic equilibrium in the cold plasma, the state of a plasma is determined by external parameters, such as electric power, pressure, gas flow rate, and internal parameters, that is, the rate constants of the reactions leading to formation or destruction of plasma species.

The knowledge of the kinetic constants is still insufficient for quantitative calculations of expected chemical behavior of most systems in the plasma. Yet semiempirical and semiquantitative models are used to predict the optimal conditions for given processes in the plasma. Plasma technology has reached the stage where it is possible to control empirically the right combination of parameters to obtain highly reproducible results, in the same system or between similar systems.

3.5 PLASMA SURFACE INTERACTIONS

The previous sections dealt with homogeneous chemical reactions occurring in the plasma bulk (Sec. 3.3.1) or heterogeneous reactions at the surfaces in contact with the plasma (Sec. 3.3.2). The existence of energetic particles and electromagnetic radiation in the plasma requires consideration of their interaction with the exposed surfaces. These physical interactions, which take place at any surface exposed to the plasma, have a significant effect on the results of the plasma treatment whether by affecting the heterogenous chemical reactions or the treated surfaces. The various particles of the plasma interacting with a solid surface exposed to it are shown schematically in Fig. 3-7.

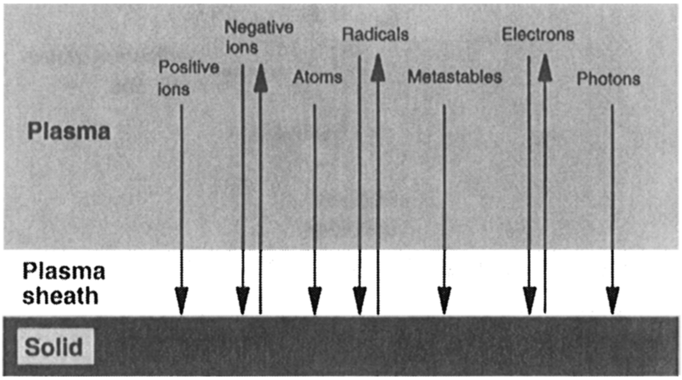

Fig. 3-7 Plasma particles interacting with a surface in a plasma.

The plasma contains energetic electrons and positive ions and also energetic neutrals. Most applications involve ions with energies in the range between 100 and 1000 eV. Bombardment of the solid surfaces with these particles can impart energy to the solid. When an energetic ion collides with a solid surface, the ion energy is transferred to the lattice atoms, creating a very-short-lived (10^{-11} to 10^{-12} sec) collision cascade of moving lattice atoms. The spatially very small, short-lived cascade can promote chemical reactions that either do not proceed at all or proceed very slowly under ambient conditions, at the temperature of the surface.

Upon contact with a surface, ions can release a significant part of their energy by producing pressure and thermal spikes. For example, thermal spikes of 3283 ^{0}K and pressures of 1.3×10^{10} Pa (1.2×10^5 atm) for 7×10^{-11} sec have been calculated for impinging ions with an energy of 100 eV [27]. According to Khaiat et al [28], it is possible to describe the neutralization of positive ions at a surface as short lived hot spots with a lifetime of the order of 10^{-14} sec. These energetic spikes obviously affect the results of the processes taking place at a surface in contact with a plasma and may be the reason for formation of *metastable materials*, such as amorphous hydrogenated silicon or diamondlike carbon. As a result of the bombardment, adsorbed species can be desorbed and substrate bonds may break causing crystal damage.

Different processes in the substrate or growing film that can be affected by the bombardment with the energetic particles are illustrated in Fig. 3-8 [29]. The figure presents the range of kinetic energies and flux densities existing in different plasma assisted techniques, while the processes caused by the bombarding particles in the surface layers of the solid are shown below the abscissa of the plot.

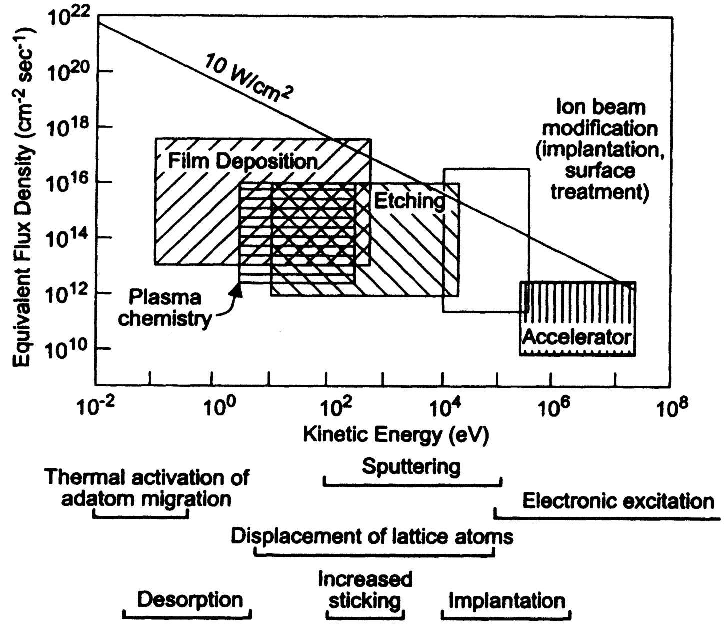

Fig. 3-8 Plasma surface interactions versus particle flux and kinetic energy (from [29], reprinted with permission).

An early detailed description of the *plasma-surface* phenomena has been given by H.F. Winters [15]. According to Winters, the plasma-surface interactions can be divided into two categories. One type of interaction takes place relatively far from the surface in which the electronic excitation energy of the particles dominates. The second type of interaction requires a much closer proximity to the surface or even penetration of the particles from the plasma into the crystal lattice and, therefore, involves the kinetic energy of the particles. Neutralization of slow ions and associated electron emission fall into the first category, while cascade effects and sputtering fall into the second category.

Excited or ionized atoms can transfer their energy near a metallic surface by undergoing an electronic transition through three different mechanisms:

1. *Deexcitation* through emission of radiation

2. Deexcitation by a two-electron *Auger process*
3. A resonance process, whereby an electron is transferred from the metal to an equivalent level in the ion

A 100-eV He^+ ion spends about 10^{-13}–10^{-14} sec within 5 Å from the surface as compared to about 10^{-12} sec for a thermal particle. Deexcitation through emission requires much longer times, of the order of 10^{-8} sec. Therefore, the probability that the deexcitation occurs through emission of radiation is very small. Nevertheless, the probabilities of neutralization near a surface in contact with the plasma are very high, close to unity as a result of the Auger and resonance processes [15]. Theoretical investigations indicate that almost all incident ions will be neutralized within a few atomic radii of a substrate by electrons produced through Auger emission processes. As a result, the particles that finally strike substrates in the plasma are mostly neutral species.

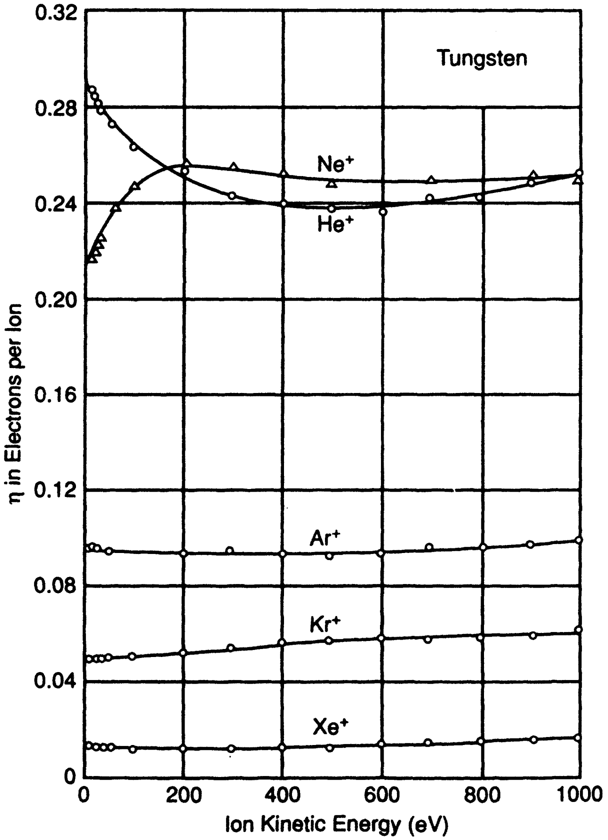

Fig. 3-9 Secondary electron yield from a tungsten surface versus ion kinetic energy (from [30], reprinted with permission).

The emission of Auger electrons leaves the solid substrate or growing film in an excited state while relaxation of the substrate from the excited state causes the generation of the secondary electron. As a result of the neutralization process, secondary electrons are emitted with a yield that is almost independent of the energy of the incident ion, but strongly dependent on its ionization potential. The *yield* is defined as the number of particles, in this case secondary electrons, emitted per arriving ion. As shown in Fig. 3-9, for a tungsten surface the yield of secondary electron emission is ~ 0.24 for He^+ and ~ 0.10 for Ar^+ ions arriving at the surface.

The emission of most of the secondary electrons is caused by the potential of the impinging ions (their electronic excitation energy), but if the kinetic energy increases above ≈ 1000 eV, *kinetic ejection* becomes dominant, and the yield for secondary electron emission increases with the kinetic energy of the ion. This is illustrated in Fig. 3-10, which presents the secondary electron yield for molybdenum, as a function of the kinetic energy of Ar^+ ions and Ar neutrals.

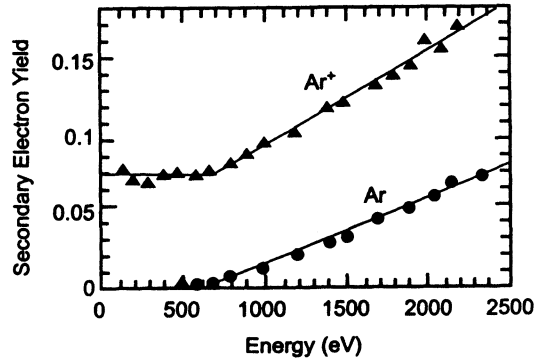

Fig. 3-10 Secondary electron yield as a function of kinetic energy for Ar and neutral atoms (from [15], reprinted with permission from S. Veprek and M. Venugopalan, eds., *Topics in Current Chemistry, Plasma Chemistry III*, Berlin: Springer-Verlag, 1980).

Ions and long-lived electronically excited metastable species of the plasma are deexcited with high probability at any surface in contact with the plasma causing concentration gradients of these species near the surface. The deexcited neutral particles are reflected from the surface with a significant fraction of their kinetic energy and with vibrational energy gained by multiatomic particles through the deexcitation process. Surfaces in the plasma are thus sources of energetic neutral particles and vibrational excited molecules.

After becoming neutralized, an ion contacting a surface exposed to the plasma begins to lose energy to the lattice of the solid. The energy can be lost in two ways:

- *Electron loss*, through electronic collisions by interactions with the electrons of the solid, resulting in excitation and ionization
- *Nuclear loss*, through the interaction of the incoming particle with the atoms of the lattice

For the ion energies encountered in a cold plasma, the electron loss is much smaller than the nuclear loss [15]. When an ion collides with a solid surface, it causes a cascade of moving atomic targets within the solid called a *collision cascade*. The nuclear loss occurs mainly through collision cascades which cause sputtering, *radiation enhanced diffusion*, backscattering of the incident ion, *ion induced chemical reactions*, or production of lattice damage.

The transfer of momentum from an energetic ion or neutral to the substrate causes heating, defect generation, and phonon interations in the surface layer. As a result, surface diffusion or adatom mobility is enhanced and improved step coverage can be obtained during film preparation by PECVD [31].

One effect of the nuclear loss is the *entrapment of gases* from the discharge in the deposited film. It was found that concentrations of argon entrapped in films can vary between 0.1 and 50 at% depending on the substrate bias. As illustrated in Fig. 3-11, significant amounts of argon were found in nickel films grown on

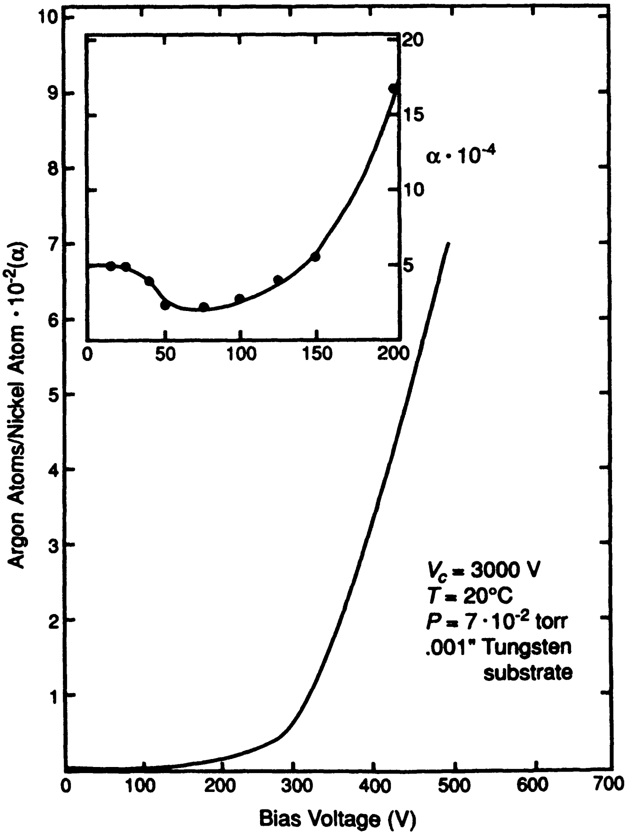

Fig. 3-11 The argon concentration in nickel films grown in a glow discharge versus bias voltage (from [32], reprinted with permission from *J. Appl. Phys.*, vol. 38, p. 3928, 1967).

substrates at negative biases bigger than 100 eV [32]. At such energies, the ions are accelerated toward the substrate and into the growing film where they are finally incorporated.

Sputtering is another important phenomenon occurring in a cold plasma. It is the ejection of material from a solid surface caused by the impingement of energetic ions. The sputtering yield, defined as the number of sputtered atoms ejected per each incident ion, depends among other parameters on the energy of the incident ion and on the ratio between the masses of the incident ion and sputtered atom. Sputtering is characterized by a threshold energy that depends on the impinging ion and the surface atoms. The sputtering threshold is in the range of 10–50 eV, as illustrated in Table 3-5 for elements bombarded with Ar^+ ions of different energies. Above the threshold energy, the sputtering yield increases with increasing ion energy.

TABLE 3-5 Threshold Values and Sputtering Yield for Argon Bombardment (from [33], reprinted with permission)

	Threshold (eV)	Ar^+ + energy (eV)				
		60	100	200	300	600
Ag	15	0.22	0.63	1.58	2.20	3.40
Al	13		0.11	0.35	0.65	1.24
Au	20		0.32	1.07	1.65	2.43
Be	15		0.074	0.18	0.29	0.80
Cr	22		0.30	0.67	0.87	1.30
Cu	17	0.10	0.48	1.10	1.59	2.30
Fe	20	0.064	0.20	0.53	0.76	1.26
Ge	25		0.22	0.50	0.74	
Mo	24	0.027	0.13	0.40	0.58	0.93
Nb	25	0.017	0.068	0.25	0.40	0.65
Ni	21	0.067	0.28	0.66	0.95	1.52
Pd	20		0.42	1.00	1.41	2.39
Pt	25	0.032	0.20	0.63	0.95	1.56
Re	35		0.10	0.37	0.56	0.91
Si			0.07	0.18	0.31	0.53
Ta	26	0.01	0.10	0.28	0.41	0.62
Ti	20		0.081	0.22	0.33	0.58
V	23	0.03	0.11	0.31	0.41	0.70
W	33	0.008	0.068	0.29	0.40	0.62
Zr	22	0.027	0.12	0.28	0.41	0.75

For conditions prevalent in most cold plasma processes, the negative self-bias of the surfaces in contact with plasma is sufficiently large to cause a certain amount of sputtering. The sputtered material can redeposit and contaminate the depositing film or the plasma treated surface.

Sputtering can also affect the plasma etching process, producing unwanted results. During plasma etching, nonetchable material sputtered from the walls of the reactor can deposit on the etched surface and prevent the etching of the area which is coated with the contaminants. As a result, surface roughening can occur or the etching reaction can stop completely [15]. The same effect can, however, be used to obtain wall tapering over steps during deposition of films by PECVD under plasma conditions that promote sputtering. Several aspects of plasma-surface interactions are discussed in greater detail in the following.

3.5.1 Ion and Electron Induced Chemical Reactions

In addition to the physical process described previously, the bombardment of a plasma treated surface with energetic particles can also affect the chemical reactions occurring at the surface and their rates. Reactions that take place at a surface exposed to the plasma can be affected by ultraviolet photons and soft X ray present in the plasma that are sufficiently energetic to break chemical bonds. However, electron and especially ion bombardments are the most effective in changing and promoting chemical reactions at the substrate. In addition to physical sputtering, ion enhanced chemistry is technologically probably the most important result of collisions of energetic ions with surfaces. Ion bombardment promotes the mixing of atoms near the surface by momentum transfer and by enhanced diffusion. This bombardment is partially responsible for the improvement in the quality of thin films that are deposited with simultaneous energetic ion bombardment.

It was also observed that surfaces subjected to ion bombardment etch much more rapidly than those kept near plasma potential. For example, in the XeF_2-Si-Ar system, gaseous XeF_2 reacts significantly with Si at room temperature [34]. But if the reaction takes place under simultaneous bombardment with ions, the probability that fluorine atoms will react to form the volatile SiF_4 and etch the Si is greatly enhanced.

This was proved by etching silicon separately with XeF_2, Ar^+ beam, and a mixture of $Ar^+ + XeF_2$. The results illustrated in Fig. 3-12 showed that the etch rate obtained with simultaneous use of XeF_2 and Ar was eight times higher than the sum of the etch rates obtained with each of the individual gases alone [35]. Similar enhancing effects produced by Ar^+ ions were observed for plasma etching of Si with F_2 or with Cl_2 and C etching with F_2.

Electron bombardment was also found to cause an enhancing etching effect. The bombardment of the surfaces exposed to the plasma by energetic electrons can also cause

- Emission of secondary electrons.
- Chemical reaction between gaseous species and the solid surface, when the reaction requires electron activation.
- Electron induced dissociation of adsorbed molecules: the bombardment with electrons of the species adsorbed on the surface can cause fragmen-

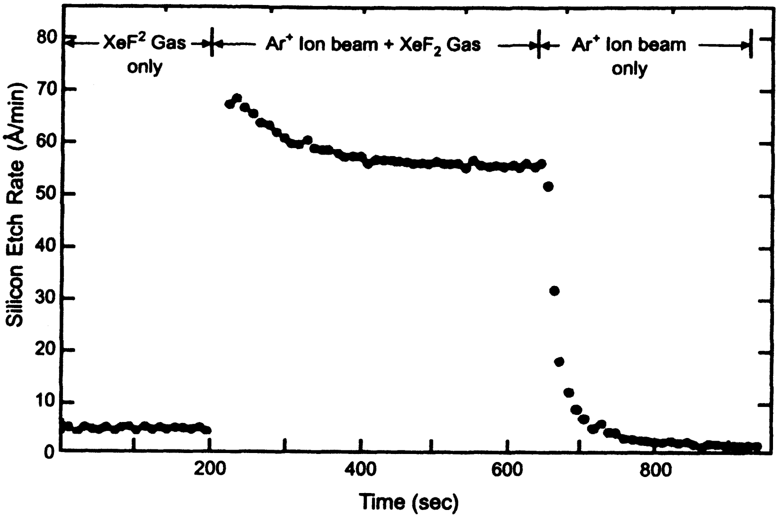

Fig. 3-12 Ion-assisted gas-surface chemistry using Ar^+ + XeF_2 on silicon (from [15], reprinted with permission from S. Veprek and M. Venugopalan, eds., *Topics in Current Chemistry, Plasma Chemistry III,* Berlin: Springer-Verlag, 1980).

tation of these species; some of the fragments will remain attached to the surface, while others will desorb into the gas phase; this process is called *electron stimulated desorption* (*ESD*).

- Lattice damage of sensitive materials.

Because the momentum of ions is much higher than that of electrons, the ion bombardment is much more effective in enhancing surface reactions than is electron bombardment.

To understand the enhancing effect produced by the impinging ions, one has to consider that steady-state etching of a solid exposed to a plasma or the film deposition go through several steps:

1. Generation of reactive species
2. Diffusion to the surface
3. Nondissociative adsorption of gas species to the solid surface
4. Surface reactions:
   a. Dissociation of adsorbed species (dissociative chemisorption)
   b. Reaction of adsorbed radicals with the solid to form adsorbed product molecules
5. Desorption of volatile species from the surface:
   a. Desorption of volatile products into the gas phase
   b. Removal of nonreactive residue from surface

6. Diffusion of volatile species away from the surface

The formation of a volatile product and its removal from the treated surface is essential to the etching process. Although in the deposition process the main product of the reaction is nonvolatile, secondary volatile reaction products may form at the surface. Removal of such volatile products and nonreacted species is important to prevent contamination of the growing film through their incorporation into it.

Steps 3 to 5 are heterogeneous stages that are affected by the substrate temperature, but their kinetics are not dependent solely on it. Bombardment of the plasma treated surface with energetic ions or electrons can affect each of these steps. For example, dissociative chemisorption may occur preferentially at defect sites produced by impinging ions. If such is the case, ion bombardment will strongly enhance the reaction rate. Ion or electron bombardment can also cause dissociation of adsorbed molecules, which would otherwise not take place.

If the formed product species are volatile, they will desorb, and the surface will be etched. If the reaction products are nonvolatile, a layer of reaction products will deposit on the surface. It may also happen that a monolayer adsorbed on the surface can prevent the dissociative chemisorption. For example, etching of Si by fluorine may be slowed by oxygen, carbon, or chlorine adsorbed on the surface. In such a situation, the cleaning of the surface through sputtering by energetic ion bombardment or through electron stimulated desorption will enable the dissociative chemisorption to take place and thus enhance the etching process. The enhancement of surface processes by ion or electron bombardment is a synergetic process.

The studies of the effects of surface bombardment by energetic particles pay special attention to etching, with emphasis on anisotropic etching. In anisotropic etching the removal of material from the plasma treated sample has to progress at a much faster rate in one direction than in the others. During processing of silicon wafers for VLSI, the dimensions of the individual lines become smaller, and anisotropic etching is required to prevent undercutting the structure underneath the mask. Anisotropic etching is also required to obtain deep trenches with straight walls.

Anisotropic etching can be obtained in most plasma systems by ion assisted gas-surface chemistry. As illustrated in Fig. 3-13, when the sample is maintained at a negative potential in plasma, positive ions bombard the surface at normal incidence, provided the dimensions of the feature are much smaller than the thickness of the plasma sheath, which is always the case in microstructure fabrication situations. Neutral species, in contrast, are incident randomly on the surface, and all surfaces are exposed to approximately equal fluxes of neutral species. Etching solely by neutrals will therefore cause isotropic etching and undercutting underneath the mask, as shown in Fig. 3-13 (a). As a result of the ion enhanced chemistry, the surface bombarded by the ions etches at a much higher rate than the lateral walls, which are not bombarded, and anisotropic etching with little undercut is obtained as illustrated in Fig. 3-13 (b).

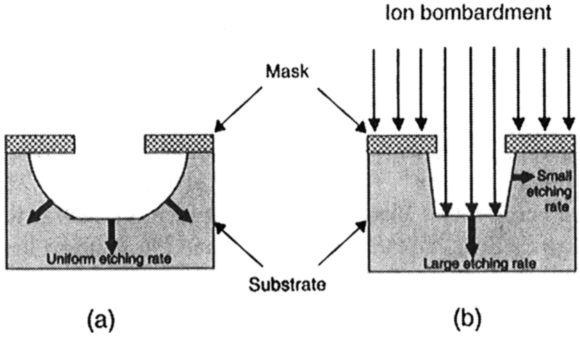

Fig. 3-13 Neutral versus ion assisted etching.

Let consider, for example, the *reactive ion etching* (RIE), of silicon by carbon tetrafluoride (CF_4). The plasma dissociates the inert fluoride into several reactive components:

$$e + CF_4 \rightarrow CF_3^+ + F + 2e \qquad (3.45)$$

The atomic fluorine that is believed to adsorb on the surface will etch the Si, though at a low rate. Bombardment of the surface with the CF_3^+ ions accelerates the etching rate. The acceleration of the etching by the CF_3^+ ions was explained in earlier proposals by assuming that the ions

- Provided additional F atoms to the etching process
- Accelerated the formation of SiF_2 by ion induced damage to the Si lattice
- Accelerated the desorption of SiF_2

However, the proposal that the accelerated reaction of F atoms with Si is caused by ion induced damage of the Si lattice is not supported by more recent experiments in which the etch rates of damaged and undamaged single-crystal Si were compared directly. Coburn et al. [21] separated the investigation of the adsorption from the following steps, that is, the formation of volatile product and the desorption of the volatile product. The authors first dosed the Si surface with fluorine, and then pumped away the fluorine from the gas phase before subjecting the fluorinated silicon surface to the ion bombardment.

Surface analysis by synchrotron photoemission of the fluorinated Si surfaces showed that the most abundant species on the surface was SiF_3 with very little SiF_4. On the other hand, SiF_4 molecules are found to be the predominant species evolved in this system during the ion assisted etching. The authors [21] therefore concluded that the ion bombardment promotes the formation of SiF_4 from the SiF_3 layer, which was already formed on the Si surface before the ion bombardment and its desorption from the surface. This conclusion was strengthened by the observation that when molecular fluorine was incident on the Si surface during bombardment with energetic ions, the etch rate observed was one order of magnitude lower compared to the etch rate observed with atomic fluorine flux. Molecular F_2 reacts with Si at much lower rates than atomic F.

The effect of the ion bombardment on plasma chemistry depends on the ratio between neutral and ion fluxes. For constant ion bombardment conditions, the etching anisotropy was found to decrease with increasing neutral flux.

The results just described emphasize that *neutral versus ion chemistry* has to be considered during the discussion of plasma-surface interactions. For example, during etching of Si with $Ar^+ + XeF_2$ a yield of the order of 25 Si atoms per Ar^+ ion was observed [21]. Since the dominant etch product in the Si-F system has been found to be SiF_4, this indicates that about 100 F atoms leave the surface for each arriving ion, provided that the XeF_2 supply is sufficiently large. The magnitude of this effect indicates that in this case the chemistry is provided essentially by the neutral species and not by the ions, because the amount of chemistry that can be provided by an ion is not sufficient to account for the observed etch rates and evolved SiF_4.

The relative importance of various ion induced phenomena can be very different for various chemical systems. For example, during etching of silicon with halide-containing gases, the diffusion of chlorine into silicon lattice is much less than that of fluorine. Consequently, ion induced mixing of the top few monolayers for enhanced reactivity is more important for the Cl-Si system than for the F-Si system.

There are also cases in which the rate of reaction between the incident gas-phase species is unaffected, or even retarded, by energetic ion bombardment, as for example the interaction of chlorine with aluminum or copper [22].

Synergetic phenomena similar to those described for etching can also be expected during deposition of films by PECVD. Creation of adsorption and nucleation sites, dissociation of adsorbed surface species, and promotion of chemical reactions due to particle bombardment can be expected especially with particle energies above 20 eV [29]. However, the different effects that the ion bombardment has on the primary processes occurring during film growth are extremely difficult to separate. The effects of the ion bombardment on the growing film as well as on the substrate are illustrated in Fig. 3-8.

3.5.2 Energy Transfer

Another aspect of the plasma-surface interactions is the transfer of energy. Energy transfer from plasma to solid surfaces occurs through optical radiation and fluxes of neutral particles and ions. The optical radiation has components in the infrared, visible ultraviolet, and sometimes soft X ray. When absorbed by a solid surface, the radiation usually transforms into heat. When the surface is a polymer, absorption of ultraviolet radiation can also break up the polymer to produce free radicals that can react with arriving plasma species.

The energy of the neutral particles is composed of kinetic, vibrational, dissociation (for free radicals), and excitation (for metastables) fractions. The dissipation of the kinetic and vibrational energy fractions causes heating of the substrate. The dissociation energy can also be dissipated through surface chemical reactions on polymers or trough surface reactions involving adsorbed species and recombinations on metals. The metastable species release their energy only through collisions that cause heating of metallic surfaces or the formation of free radicals on polymers [5].

The energy of the ion flux is composed of kinetic, vibrational, and electronic fractions. The ions are accelerated toward the surfaces exposed to the plasma that are negatively self- or externally biased relative to the plasma. The ion bombardment can affect the properties of the deposited film if the ion energy is sufficiently high. In an RF plasma, the kinetic energy with which an ion reaches the electrode depends on the ratio between the distance passed by the ion during half a cycle and the width of the plasma sheath. This distance is a function of the ion mobility, the sheath field, and the frequency of the electromagnetic field sustaining the plasma. If the distance traveled by the ion during half a cycle is larger than the width of the sheath, the ion can impact the electrode with energies equivalent to a DC discharge of a potential approximately equal to the RF amplitude. If the distance is much smaller than the sheath width, the equivalent DC voltage can be up to a factor of 3 less than that of the surface bias. On electrically floating surfaces, the ions arrive usually with energies up to 5 eV and can cause ablation or electrostatic charging of the surface. On biased surfaces the ions can arrive with kinetic energies of hundreds of volts and dissipate it by causing heating and sputtering of the surface.

The ionization energy is released by neutralization and is dissipated by either heating of metals surface or formation of free radicals on polymers.

3.5.3 Effects on Film Growth

The chemical reactions in the plasma and at the solid surface are determining the composition of the final product of a plasma process. However, in contrast to thermal systems in thermodynamic equilibrium, the plasma-surface interactions, in addition to enhancing the processes which take place at the surface, also affect the structure and properties of the plasma treated surfaces.

Ion impact that occurs on the negatively biased surfaces can affect the physical properties of the material. During deposition, it can cause densification and increased oxidation resistance of the films. It might minimize or eliminate columnar microstructures in metallization layers used in electronic devices. It can improve the quality of films grown under simultaneous ion bombardment, alter the state of stresses in the growing film, improve adhesion between film and substrate, or enhance conformal coverage [36]. Ion impact in PECVD can also cause enhanced diffusion, collisional mixing, and the formation of metastable materials, such as amorphous hydrogenated silicon or amorphous hydrogenated carbon (diamondlike carbon).

Following are a few examples that illustrate the effects of the plasma-surface interactions on the deposition of films and their properties.

- Enhancement of surface diffusion by ion bombardment during PECVD deposition of coatings on nonplanar surfaces results in improved step coverage [31, 37].
- The substrate temperature required to obtain crystalline coatings can be lowered using PECVD. Thus the amorphous to crystalline transition temperature could be lowered during deposition of silicon to ~ 300 °C [38] and single-crystal ZnO films have been obtained by PECVD at temperatures as low as 200 °C [39].
- Lowering the temperature of epitaxial deposition can be accomplished using low-energy ion bombardment during PECVD [40, 41].
- During deposition of diamondlike carbon by RF PECVD, polymerlike films are obtained on the grounded electrode, which is at low negative self-bias relative to the plasma, while hard diamondlike carbon films are obtained on the powered electrode, which is generally at larger negative bias.
- The deposition rate of diamondlike carbon on the powered electrode of a parallel plate reactor was found to be up to four times faster than that on the grounded electrode [42, 43].
- A similar effect has been observed in plasma polymerization where a higher rate of deposition was found on the powered electrode as compared to the one on the walls of the reactor [44, 45].
- It was also found that for both amorphous hydrogenated silicon and diamondlike carbon the anodic material has a higher hydrogen concentration and, consequently, a larger band gap than the cathodic material [46].
- Plasma nitriding of metals takes place at much higher rates and lower temperatures than does conventional thermal nitriding, and the composition and structure of the nitrided layers can be tailored by controlling the plasma process parameters.

3.5.4 Plasma Induced Damage

The bombardment of the substrate with energetic particles during cold plasma treatment can produce etch directionality and also required changes in the properties of the material. However, if the energies of the particles are high or the fluxes are large, damage can occur in existing films or substrates. Plasma induced damage can occur, especially during reactive ion etching when the substrate is negatively biased at relatively high bias of several hundred volts and is therefore exposed to bombardment of high-energy ions. The damage is caused through bond breaking by the bombarding particles and formation of defects in the surface layer of the substrate. Thus damage was observed in silicon wafers after reactive ion etching in CF_4 plasma, to which hydrogen was added to cause etch selectivity of oxide to silicon [47]. The damage was explained as being caused by physical bombardment of the wafer by hydrogen ions.

The study [47] indicated that the defect formation is not chemical but a result of bombardment of the surface with hydrogen ions. The damage consisted mainly of displaced Si atoms that migrated several nanometers and reorganized into interstitial dislocation loops. The defects are propagated during thermal oxidation into the substrate in the form of stacking faults below the oxide-silicon interface. The defects produced by the hydrogen-containing plasma caused the degradation of the lifetime of MOS capacitors. The degree of damage can be reduced by decreasing the exposure time to the hydrogen-containing plasma.

A similar study was performed on silicon wafers reactively ion etched in a CF_4 + 40% H_2 plasma. The RIE was performed at a pressure of 25 mtorr and at a substrate self-bias of $-$ 425 V. The etching caused changes in the silicon wafer which consisted of [48]:

- A film containing carbon and fluorine, less than 50 Å thick deposited onto the silicon.
- A layer of ~ 30–50 Å heavily damaged, amorphized silicon was formed as a result of bombardment with heavy energetic particles which caused collision cascades.
- Hydrogen implantation (about 5%) to depth in excess of 200 Å; this layer was less damaged than the silicon layer immediately adjacent to the surface. Raman studies showed that the hydrogen is bonded to the silicon lattice.

A diagram of the damaged layer produced by the exposure of silicon to the plasma is shown in Fig. 3-14.

The changes caused in the material by ion bombardment resulted in the degradation of the electronic properties of the silicon as following:

- Degradation of the minority carrier lifetime
- Changes in the barrier height and ideality factor of Schottky barriers formed on dry etched silicon
- High contact resistance in contact hole etching
- Deterioration of the oxide quality (interface state density, dielectric strength) of thermal SiO_2 films grown on dry etched substrates

Similar behavior was observed in etching of silicon with fluorine containing gases. Fluorine was observed to a depth of 2000 Å with a maximum of 4% at a depth of 500 Å [49].

During ion bombardment, impurities from the plasma can penetrate the substrate either by implantation or through enhanced diffusion. Hydrogen atoms are especially prone to penetrate the substrate because of their small size. Ion bombardment can cause formation of point defects in the crystal lattice. The plasma can also cause contamination of the substrate with material sputtered from the walls of the reactor or the electrodes [50].

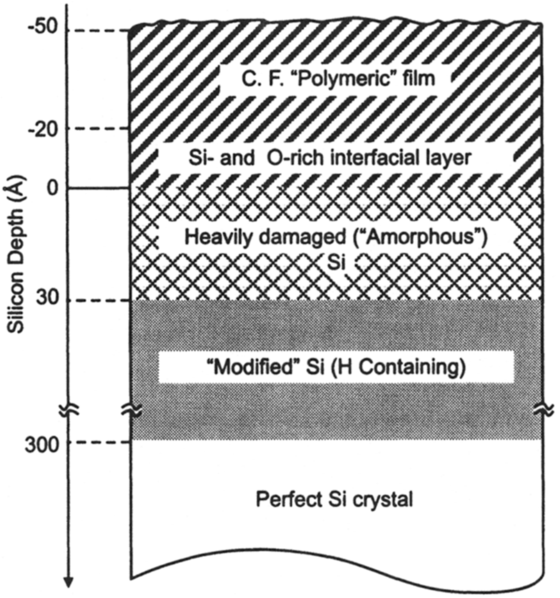

Fig. 3-14 Diagram of changes of Si near-surface region caused by $CF_4 + H_2$ reactive ion etching (from [48], reprinted with permission).

In addition to energetic ions and electrons the plasmas contain significant amounts of ultraviolet radiation, which can extend in energy to several tens of electron volts per photon. In dielectrics such as SiO_2 characterized by a bandgap smaller than 9 eV, the ultraviolet radiation can create defects that are detrimental to the surrounding circuitry. Positive fixed charge densities were observed in thermal oxides exposed to industrial plasmas of O_2 or SF_6, reaching values of 2×10^{17} cm^{-3} in a 1-kW microwave plasma at 2 mtorr [51].

Charge accumulation can occur on insulating layer, such as gate oxide, exposed to a cold plasma. At sufficiently high accumulation, the charges may cause electrostatic breakdown of the dielectric. Exposing a wafer containing MOS devices to a plasma discharge during patterning of polygate structures may cause damage to the device due to charge accumulation. It has been found [52] that at 13.56 MHz, the charge that can be transferred to the wafer is so small that it is unlikely that the gate will reach a level where electrical breakdown will occur. If, however, the frequency is low or a DC supply is used, breakdown of the oxides may appear. Samples subjected to a low-frequency or DC plasma were found to exhibit an increase in the density of states at the oxide semiconductor interface [52].

Recent studies [29] show that substrate damage is much smaller in films deposited by PECVD than in films deposited by sputtering. This may be due to the lower ion energies in PECVD plasmas as compared to those in sputtering plasmas. The difference in ion energies is caused by higher pressures and lower-power densities in PECVD. Substrate temperatures above 200 °C, generally used in PECVD, can also cause annealing of some of the defects during the deposition process. The substrate damage following plasma etching was also found to be greater than after plasma deposition. This may be a result of the fact that, while in PECVD the substrate is exposed to the plasma only for a short time at the start of the deposition, in etching the substrate is exposed to the plasma at the end of the process.

3.6 QUESTIONS

1. What type of reactions can cause dissociation of molecules in a low-pressure plasma reactor?
2. a. Describe the different ionization reactions that can occur in a plasma reactor.
   b. How are negative ions formed in a cold plasma and in what type of gases?
3. What reactions result in recombination of plasma species?
4. Which plasma reactions are associated with emission of electromagnetic radiations?
5. Describe the difference between ion-molecule and radical-molecule reactions. Which type usually dominates in cold plasmas and how can the overall process be affected by the relative contribution of each type of reaction?
6. Where do heterogeneous reactions take place in a plasma? Exemplify.
7. What processes take place at a surface in contact with a plasma? How can these processes cause contamination of a coating deposited in a plasma?
8. What type of material damage can be induced by exposure to a cold plasma?

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