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ture conditions (>850°C) limit its suitability. Plasmaenhanced CVD (PECVD) has received substantial attention in recent years because it grows films of metals, semiconductors, and insulators at relatively low temperatures on temperature-sensitive substrates. Low-temperature deposition methods are essential in minimizing defect formation and solid-state diffusion between deposited layers. The fact that insulating films for diffusion masks, interlayer dielectrics, and passivation layers are deposited at low temperatures, so that previous steps are not affected, is extremely important for this industry. The plasma, also known as a glow discharge, generates energetic electrons (1 eV to 10 eV) (1), which interact with and ionize gaseous precursor molecules to form chemically reactive radicals and ions. These active species react either in the gaseous stream in a homogeneous reaction or migrate to the substrate surface where they undergo a heterogeneous reaction to form the film. Reaction byproducts evolve and are carried away in the gas stream. The inherent applicability of the plasma deposition process to uniform deposition over large areas is basically a result of the relative ease by which uniform electric fields are created over large areas. PECVD is currently being used to produce thin films of materials such as amorphous silicon (a-Si), silicon nitride, silicon dioxide, silicon carbide, boron nitride, and diamondlike carbon coatings (DLC).

The conductivities of the substrate and the growing film determine the method of plasma creation. Conductive materials are adequately deposited by dc plasma generation. However, dielectrics and semiconductor materials very commonly use RF plasma generation. Other ways of plasma generation, such as by microwave or laser incorporated with magnets are being developed. We begin by reviewing the basic physics and chemistry of nonequilibrium glow discharges.

BASIC PRINCIPLES OF PECVD

A glow discharge is defined as a partially ionized gas composed of equal volume concentrations of positively and negatively charged species and different concentrations of species in the ground state (2). The processing glow discharge or plasma is produced and driven by external power supplies from dc up to radio frequencies of about 10 GHz and in power up to 30 kW. Figure 1 shows a schematic of the components of a typical apparatus for PECVD (3). There are basically three classes of techniques used to create and sustain the type of plasmas used for thin film growth (4). The first involves applying a high voltage to a metal electrode or set of electrodes within the discharge chamber. The electrodes that are normally in the form of parallel plates are said to have a diode configuration. Devices that use this kind of configuration include dc and RF diodes, magnetrons, and some PECVD systems. The second class of plasma generation technique involves applying electric fields, typically through an insulator. The high electric field is used to help break down the gas and cause ionization. Inductively and capacitively coupled barrel reactors and electron cyclotron resonance (ECR) reactors are examples of devices using this technique. The third class creates and sustains the plasma by injecting large currents of electrons emitted thermionically from a filament or related electron source and then accelerated into the plasma. The accelerated electrons cause ionization and maintain the plasma.

PLASMA DEPOSITION

Plasma deposition is a processing technique that has gained popularity in the microelectronics industry in recent years because it operates at relatively low temperatures ($<250^{\circ}$ C). Chemical vapor deposition (CVD) has been the primary method of device manufacture, but high operating tempera-

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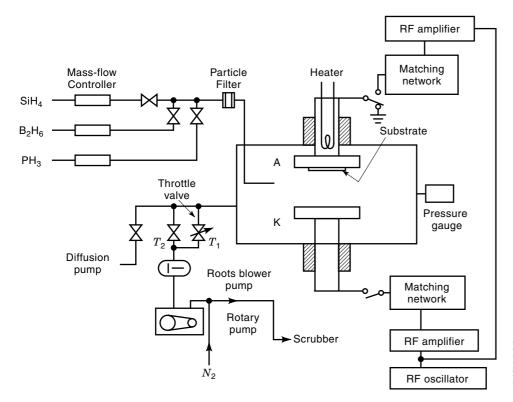


Figure 1. Typical components of a PECVD apparatus consist of a reactant flow control unit, a plasma reactor, and low and high vacuum pumps (3).

Because dielectric and nonconducting materials are mostly used in the microelectronics industry, RF glow discharge is discussed more than dc glow discharge.

Potentials Experienced in RF Glow Discharges

RF glow discharges used to deposit thin films operate at frequencies between 13.56 MHz and 50 MHz and at pressures between 10 Pa to 300 Pa. The plasma density (i.e., the density of ions and free electrons) is in the range of 10^8 to 10^{12} cm⁻³. The degree of ionization is typically $<10^{-4}$ implying that most species in the glow are neutral on the order of approximately 10^{15} to 10^{16} cm⁻³. High-energy electrons with energies on the order of 10 to 30 eV generate the reactive species. The average electron energy (1 eV to 10 eV) is considerably higher than the average ion energy (~ 0.04 eV) (1,5). The combined density of condensable species, namely, neutral radicals and ions, is small relative to the gas density, and the density of condensable neutrals is much higher than that of charged particles. Therefore, the film is predominantly formed by bonding neutral radicals to the surface of the growing film.

The potentials of glow discharges used in PECVD are (1) the plasma potential, (2) the floating potential, and (3) the sheath potential. The plasma potential V_p is the potential of the glow region of the plasma, which is normally considered equipotential. It is the most positive potential in the chamber and is the reference potential for the glow discharge. The floating potential V_f is the potential at which equal fluxes of negatively and positively charged species arrive at an electrically floating surface in contact with the plasma. The resultant potential is represented approximately by the following expression (5):

$$V_{\rm p} - V_{\rm f} = \frac{kT_{\rm e}}{2e} \ln\left(\frac{m_{\rm i}}{2.3m_{\rm e}}\right) \tag{1}$$

where T_e is the electron temperature, e is the unit electron charge, and m_i and m_e are the ion and electron mass, respectively (2,5,6). Most sputtering threshold energies range from 20 to 40 eV (7). Therefore it is desirable to operate the plasma with a $(V_p - V_f)$ less than 20 eV to avoid sputtering material off the reactor wall, which may otherwise lead to film contamination. Between the electrode and the glow discharge there is a narrow dark region or sheath (typically 0.01 cm to 1 cm, depending primarily upon pressure, power, and frequency) called the dark space. Within this region, the positive ions are accelerated to the electrode or substrate surface, and secondary electrons emitted from the electrode surface are accelerated out into the glow discharge. The difference between the potential at the surface and the plasma potential determines the maximum energy with which the positive ions bombard the surface and electrons enter the glow discharge. The potential across the sheath is called the sheath potential.

The reason for the different potentials within a plasma system becomes obvious when electron and ion mobilities are considered. Imagine applying an RF field between two plates or electrodes positioned within a low-pressure gas. On the first half-cycle of the field, one electrode is negative and attracts positive ions. The other electrode is positive and attracts electrons. Because the mobility of the electrons is considerably greater than that of positive ions and also considering the high frequencies used in RF discharges, the flux of electrons or current is much larger than that of positive ions. This situation depletes electrons in the plasma and results in a positive plasma potential. On the second halfcycle, a large flux of electrons flows to the electrode that previously received the small flux of ions. The plasma potential is nearly uniform throughout the observed glow volume in an RF discharge, although a small electric field directed from the discharge toward the edge of the glow region exists.

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There are two distinct regions, low- and high-frequency regimes in the frequency of the input power. The boundary between the two regions is given by the critical frequency f_c , which is expressed as (3)

$$f_{\rm c} = \frac{\mu_{\rm i} E_0}{\pi l} \tag{2}$$

where μ_i is the ion mobility, E_0 is the amplitude of the ac electric field, and l is the electrode spacing. The critical excitation frequency f_c is estimated to be between 10 kHz to 100 kHz, below which both ions and electrons respond to the alternating electric field. Beyond f_c , ionic species no longer respond as the electrons do. The relatively heavy ions do not respond to the field by significant displacement and therefore are considered immobile.

Generation of Active Species

As electrons and molecules undergo collisions within the plasma, various excited and metastable states of species are generated. There are two kinds of collision processes generating these species, elastic and inelastic collisions. Elastic collisions between energetic electrons and neutral or ionized species result in little transfer of energy to the atom or ion because of the large mass difference between the species. Inelastic collision processes, on the other hand, lead notably to ionization and generate species in electronically excited states. The ionization process is expressed as

 $Ionization \qquad \qquad e+X \to X^+ + 2e^-$

where X is a gaseous species and e is an electron. An additional electron is generated to contribute to maintaining the plasma. Another form of ionization termed dissociative ionization occurs, in which a molecule is dissociated and one of the atoms is ionized. This process requires a little more energy and is expressed as

Dissociative Ionization

$$e + X_2 \rightarrow X^+ + X + 2e$$

The threshold energy for ionizing Ar is 15.8 eV (8). In RF plasmas, the high frequency used is responded to appreciably by the electrons which pick up enough energy from the field to fragment, ionize, and excite the gas molecules. The excitation of an atom or ion, which normally has a very short lifetime, is expressed as:

Excitation
$$e + X \rightarrow X^* + e$$

The excitation may be rotational, vibrational, or electronic. The threshold energy for excitation of Ar is 11.56 eV (8). In the case of inert gases, some excited atoms may have a longer lifetime of perhaps many milliseconds and during that time may collide with a ground-state atom. This collision that excites or sometimes ionizes that atom is known as the Penning process and is described by:

$$\begin{array}{ll} \mbox{Excitation} & X^* + Y \rightarrow X + Y^* \\ \mbox{Ionization} & X^* + Y \rightarrow X + Y^+ + e^- \end{array}$$

where X and Y are arbitrary species. Some species, such as He and Ne, are intentionally added to plasmas to enhance

the Penning process. Other types of collisional reactions are dissociative attachment and dissociation. The process of dissociative attachment can be represented by the following reaction:

Dissociative Attachment

$$\mathrm{e} + \mathrm{X}_2 \rightarrow \mathrm{X}^- + \mathrm{X}^+ + \mathrm{e}^-$$

The process of dissociation is also represented by the following collisional reaction:

ssociation
$$e + X_2 \rightarrow 2X + e^-$$

The collisional processes in order of increasing energy requirement are (1) excitation, (2) dissociative attachment, (3) dissociation, (4) ionization, and (5) dissociative ionization. The reactive species generated in the plasma have lower energy barriers to physical and chemical reactions than the parent species and consequently react at lower temperatures.

Film Deposition in PECVD

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The process of film deposition in PECVD can be broken down into the following eight primary steps:

- 1. Transport of the reactants to the deposition region
- 2. Generation of condensable reactive species
- 3. Diffusion of reactant species to the substrate surface
- 4. Adsorption of the reactants onto the substrate surface
- 5. Physicochemical reactions leading to the solid film and reaction by-products
- 6. Desorption of volatile by-products
- 7. Diffusion of volatile products away from the surface into the main gas stream
- 8. Transport of by-products away from the desorption region and out of reaction chamber.

Figure 2 (9) shows a schematic of the processes involved in PECVD. The predominant flux impinging onto the substrate

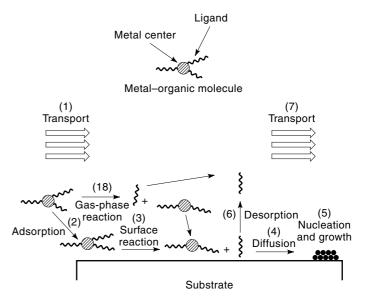


Figure 2. During PECVD the reactants are transported in the gas phase to the substrate surface, a reaction generates the required material to be deposited, and the byproducts are desorbed and exhausted from the chamber (9).

surface is inferred to be radicals rather than ions, and the thin film formation process might be controlled either by the generation rate of radicals or by the surface reactions among radicals. As indicated in the preceding section, various collisional processes contribute to the generation of the required condensable reactive species. The rate at which inelastic collisions generate excited species, ions, free radicals, etc., is estimated by a reaction rate equation (10). For example, the rate at which X^* is created from the excitation reaction

Excitation
$$e + X \rightarrow X^* + e^-$$

is given by:

$$\frac{d[X^*]}{dt} = k_1[X][e] \tag{3}$$

where $d[X^*]/dt$ is the rate of formation of X^* , k_1 is the reaction rate coefficient, [X] is the concentration of species X, and [e]is the electron concentration. Because only high-energy electrons participate in inelastic collisions, the rate constant must be defined in terms of the electron velocity and the inelastic collision cross section. The cross section of an electron/particle inelastic collision is proportional to the probability that this inelastic collision occurs and is a function of the electron energy. The rate coefficient k_i can be calculated by using the following equation (11):

$$k_i = \int_0^\infty \left(\frac{2E}{m_{\rm e}}\right)^{1/2} \sigma_{\rm i}(E) f(E) \, dE \tag{4}$$

where E is the electron energy, m_e is the electron mass, σ_i is the collision cross section of reaction i and is a function of E, and f(E) is the electron energy distribution function that gives the fraction of free electrons having a given energy. The integration is carried out over all possible electron energies. The square root term in Eq. (4) is the electron velocity. If an accurate expression for f(E) and the electron collision cross section for the various gas-phase species present are known, the reaction rate coefficients and reaction rates can be calculated theoretically. Unfortunately, such information is generally unavailable for many molecules used in plasma deposition.

Dissociation Reactions of Reactants

The photolytic decomposition of a gas can provide useful insights to the most probable primary processes in the glow discharge. The reaction steps of representative gases utilized for producing Si_3N_4 , SiO_2 , a-Si, and BN thin films are summarized in Table 1 (3,12–15). The standard heats of formation of gas molecules and their fragments, shown in Table 2 (3), are useful in predicting the possible electron-impact dissociation reactions.

Electron impact dissociation of SiH_4 produces primary reaction products as follows:

$$\mathrm{SiH}_4 \rightarrow \mathrm{SiH}_2 + \mathrm{H}_2 \qquad (\Delta H = 2.2\,\mathrm{eV}) \tag{a}$$

$$\operatorname{SiH}_4 \to \operatorname{SiH}_3 + \mathrm{H}$$
 ($\Delta H = 4.0 \,\mathrm{eV}$) (b)

$$\operatorname{SiH}_4 \to \operatorname{Si} + 2\operatorname{H}_2$$
 ($\Delta H = 4.4 \,\mathrm{eV}$) (c)

$${\rm SiH}_4 \rightarrow {\rm SiH} + {\rm H}_2 + {\rm H} \quad (\Delta H = 5.9\,{\rm eV}) \eqno(d)$$

The differences in the energy requirement for the various dissociation reactions determine the ease with which each reaction occurs. The most common primary reaction is Eq. (a) and the least probable occurrence will be Eq. (d). The enthalpy of formation ΔH is calculated from Table 2. It is inferred that the plasma decomposition of NH₃ occurs through the following primary step (3):

$$NH_3 \rightarrow NH + H_2 \quad (\Delta H = 3.9 \text{ eV}) \quad (e)$$

$$NH_2 \rightarrow NH_2 + H \quad (\Delta H = 4.5 \text{ eV}) \quad (f)$$

Secondary reactions between neutral fragments and reactant gas also take place in the plasma, such as (3)

$$H + SiH_4 \rightarrow SiH_3 + H_2$$
 ($\Delta H = -0.5 \,\mathrm{eV}$) (g)

$$\mathrm{H} + \mathrm{Si}_{2}\mathrm{H}_{6} \rightarrow \mathrm{SiH}_{3} + \mathrm{SiH}_{4} \qquad (\Delta H = -0.6\,\mathrm{eV}) \qquad (\mathrm{h})$$

$$\mathrm{H} + \mathrm{NH}_3 \rightarrow \mathrm{NH}_2 + \mathrm{N}_2 + \mathrm{H}_2 \quad (\Delta H = -0.04 \,\mathrm{eV})$$
 (i)

Similarly, radical-molecule reactions also take place (3):

$$\begin{split} \mathrm{SiH}_2 + \mathrm{SiH}_4 &\to \mathrm{Si}_2\mathrm{H}_6 \quad (\Delta H = -2.1\,\mathrm{eV}) \quad (j) \\ \mathrm{NH} + \mathrm{NH}_3 &\to \mathrm{N}_2\mathrm{H}_4 \quad (\Delta H = -2.4\,\mathrm{eV}) \quad (k) \end{split}$$

These reactions are among many that form the basis of the deposition process in PECVD of $\mathrm{Si}_3\mathrm{N}_4$, SiO_2 , and amorphous Si.

Homogeneous and Heterogeneous Processes

In RF systems, gas-phase collisions generate condensable reactive free radicals, metastable species and ions, and thus encourage the occurrence of gas-phase (homogeneous) reactions. These reactions lead to powder formation, which is detrimental to film formation. Examples of reactant combinations that lead to homogeneous reactions are silane and oxygen (fast reaction) and silane and nitrous oxide (slow reaction) mixtures, in addition to many hydride-fluoride gas mixtures. There are also the inherent complications of gas-phase reactions between the components for activation and the different gas and plasma kinetics of the gases in the mixture. A combination of electrical power, pressure, and flow rate parameters are chosen to obtain a high deposition rate without any powder formation in the reaction zone.

Heterogeneous processes result from interactions taking place between the elements in the plasma and the substrate surface. Following is a summary of the primary processes of interest in plasma deposition (1):

- Ion-surface interactions
 - 1. Neutralization and secondary electron emission
 - 2. Sputtering
 - 3. Ion-induced chemistry
- Electron-surface interactions
 - 1. Secondary electron emission
 - 2. Electron-induced chemistry
- Radical- or atom-surface interactions
 1. Film deposition

Although vacuum-UV photons and soft X rays in the plasma are sufficiently energetic to break chemical bonds, electron and, particularly, ion bombardments are the most effective methods of promoting surface reactions (16). Ions impinging

Absorption Wavelength (nm)					
SiH_4	150	200	$SiH_2 + 2H$	$SiH_2+SiH_4\rightarrow Si_2H_6$	12
			$SiH_3 + H$	${ m H}+{ m SiH_4} ightarrow{ m SiH_3}+{ m H_2}$	
$\mathrm{Si}_{2}\mathrm{H}_{6}$	210		$SiH_2 + SiH_3 + H$	$\mathrm{H}+\mathrm{Si}_{2}\mathrm{H}_{6} ightarrow\mathrm{H}_{2}+\mathrm{Si}_{2}\mathrm{H}_{5}$	13
			$SiH_3 + SiH + 2H$	$\mathrm{H}+\mathrm{Si}_{2}\mathrm{H}_{6} ightarrow\mathrm{SiH}_{3}+\mathrm{SiH}_{4}$	
			$Si_2H_5 + H$		
PH_3	220	$<\!\!200$	$H + PH_2$	$\mathrm{H}+\mathrm{PH}_3 ightarrow \mathrm{PH}_2+\mathrm{H}_2$	14
B_2H_6	200	180	$BH_3 + BH_3$		14
NH_3	210	190	$NH_3 + H$		15
			NH + 2H	$\rm NH$ + $\rm NH_3 \rightarrow N_2H_4$	
O_2	242	140	O + O	$\mathrm{O}+\mathrm{O}_2+\mathrm{M}^b ightarrow\mathrm{O}_3+\mathrm{M}^b$	14
O_3	300	250	$O + O_2$	$O + O_3 \rightarrow O_2 + 2O \text{ or } 2O_2$	14
HCl	200	150	H + Cl	$H + HCl \rightarrow H_2 + Cl$	14
				$\mathrm{Cl} + \mathrm{Cl} + \mathrm{M}^b \rightarrow \mathrm{Cl}_2 + \mathrm{M}^b$	
N_2O	210	180	$N_2 + O$	$\mathrm{O}+\mathrm{N}_2\mathrm{O} ightarrow\mathrm{N}_2+\mathrm{O}_2$	14
				${ m O}+{ m N_2O} ightarrow2{ m NO}$	
H_2O	180	165	$H_2 + O$	$O + H_2 \rightarrow OH + H$	14

Table 1. Photoprocesses of Typical Gases Used in the Production of ${\rm Si}_3{\rm N}_4,\,{\rm SiO}_2,$ a-Si, and $B{\rm N}^a$

^a Ref. 3.

^b M is a nonabsorbing, foreign gas.

on the surface influence the kinetics of network formation and the nature of the resulting film. Radiation damage during PECVD displaces atoms generating vacancies, interstitials, dislocation loops, and stacking faults. Such damage degrades material properties and alters the characteristics of fabricated devices. A fundamental understanding of gas-phase plasma chemistry and physics, along with surface chemistry modified by radiation effects, is needed to define film-growth mechanisms. The complex interactions involved in PECVD

 Table 2. Standard Heat of Formation for Various Species of

 Gas Molecules and Their Fragments^a

Species	Standard Heat of formation (eV)	
Н	2.27	
\mathbf{H}_2	0	
Si(g)	4.69	
SiH	3.90	
${ m SiH}_2$	2.52	
${ m SiH}_3$	4.00	
$SiH_4(g)$	0.32	
$\mathrm{Si}_{2}\mathrm{H}_{6}$	0.74	
Ν	4.92	
NH(g)	3.44	
$NH_2(g)$	1.75	
$NH_3(g)$	-0.48	
N_2H_4	0.53	
B(g)	5.78	
BH	4.50	
BH_2	2.08	
$BH_3(g)$	1.11	
P(g)	3.27	
$_{\rm PH}$	2.63	
$PH_3(g)$	0.06	
NO	0.94	
N_2O	0.85	
0	2.59	

are outlined in Fig. 3 (17). If the basic or microscopic plasma parameters (neutral species, ion, and electron densities; electron energy distribution; and residence time) are controlled, the gas-phase chemistry can be defined. Many macroscopic plasma variables (gas flow, discharge gas, pumping speed, RF power, frequency, etc.) can be changed to alter the basic plasma conditions. Electrode and chamber materials also alter the chemistry of glow discharges because of chemical reactions on or with the surface. Synergism between these numerous processes results in specific film-growth mechanisms. Ultimately, these factors establish film composition, bonding structure, and thus film properties.

EQUIPMENT USED IN PECVD

Predicting deposition rates and uniformity require detailed understanding of thermodynamics, kinetics, fluid flow, and mass transport phenomena for the appropriate reactions and reactor design. The plasma deposition process commonly involves using potentially hazardous gases. This requires extreme precautions, such as locating the gases in vented gas cabinets to avoid gas accumulation. The hazard of using silane, the main processing gas in the plasma deposition process, is its rather unpredictable pyrophoricity rather than toxicity (18). However, the pyrophoric tendency of silane can be used with advantage to reduce the toxic hazard of dopant gases, such as diborane and phosphine. It is common practice to acquire the toxic dopant gases at relatively low concentrations (100 ppm to 1%) prediluted in silane, on the premise that the dopant gas will oxidize rapidly in the silane flame which results from a large exposure. Excess flow shut-off valves are also incorporated to close automatically if the gas flow exceeds a preset limit. These shut-off valves are located between the gas tank and the pressure regulator on the tank. Lines are often dedicated to one specific gas and are led to a gas-mixing manifold where the various individual gases are mixed after metering and before entering the reactor. Mass flow controllers are generally used to gauge and control the gas flow into the plasma reactor because, in contrast to rotameters and needle valves, they are independent of the pressure of the gas at the inlet or the outlet. Different types of reactors for the plasma deposition process (PECVD) are discussed in a later section. Because the process forms particles, large filters are recommended between the reaction chamber and the exhaust pumping system. A variety of devices, such as scrubbers, burn boxes, activated carbon filters, and high velocity ejectors, are used to reduce the hazards of the exhaust gases. Nitrogen at flow rates exceeding the highest process gas flow by at least a factor of 10 (18), is commonly used to force the exhaust effluent from the high-pressure side of the mechanical pump through scrubbing and filtering devices. The potentially hazardous nature of the reaction materials requires placing interlocks to take appropriate action automatically in incidents and emergencies. A combination of electrical power, pressure, and flow rate parameters has to be chosen to obtain a high deposition rate without any powder formation in the reaction chamber.

PECVD Reactor Systems

PECVD reactors operate mostly on a batch scale, but continuous reactors are being developed to increase throughput. The batch reactors are (1) the radial-flow batch reactor and (2) the tubular reactor. These reactors are designed to be either coldor hot-walled. In the radial-flow batch reactor, the plasma is generated between two parallel, circular electrodes as shown

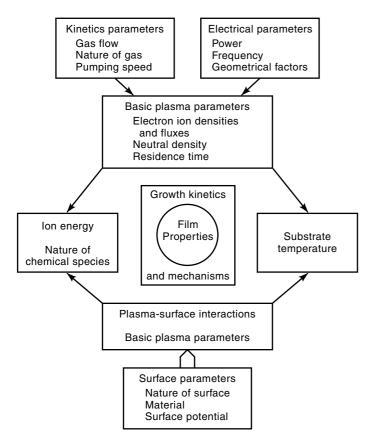


Figure 3. The properties of the films are controlled by complex interactions between the plasma parameters, kinetics of film formation, and plasma-surface interactions (17).

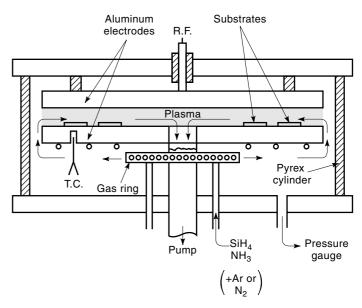


Figure 4. A schematic of the cold-wall radial-flow, plasma-enhanced CVD reactor after Reinberg has the reactants introduced from the periphery of the substrate holder and exhausting in the center (19).

in Fig. 4 (19). This is known as the Reinberg design. The wafers are loaded onto the lower, electrically grounded electrode. The powered electrode in this cold-wall reactor is connected to the high frequency RF power generator through an impedance-matching network. The reactants are introduced from the gas ring, enter the plasma region (i.e., the region between the electrodes) at its outer edge, and flow radially inward toward a pumping port at the center of the lower electrode. Various variations of this design have since been introduced. In the modified Reinberg design developed by Applied Materials, the gas is introduced in the center of the circular electrodes and exhausted at the periphery. Figure 5(20) shows a further improvement on the radial flow batch reactor in which a perforated upper electrode is incorporated for more uniform gas distribution. This design was developed to cater to gas mixtures of low concentrations of the active components, such as 2% SiH₂ in N₂. The perforation helped solve the problem of reactant gas depletion before traversing the full cross section of the electrode, thus resulting in nonuniform film formation.

The tubular reactor, shown in Fig. 6 (20), consists of a tube of fused quartz within a resistively heated furnace (hot-wall reactor). Vertically oriented rectangular graphite plates carry the wafers in slots, and the wafer surface acts as one electrode. Every other slab is connected to the same RF power terminal as shown schematically in Fig. 6. The glow discharge is generated capacitively between adjacent parallel-plate electrodes. The reactants are directed along the axis of the chamber tube and between the electrodes. Pulsing of the RF power improves deposition uniformity in this reactor. Robotic machinery is used for automatic cassette-to-cassette loading and unloading of wafers, and cantilevers are designed for inserting and withdrawing the electrode units. Contamination by particles has been significantly reduced by these techniques.

A continuous-processing, radial, cold-wall reactor by Novellus (21) sequentially indexes each wafer through several deposition stations on a resistance-heated substrate plate

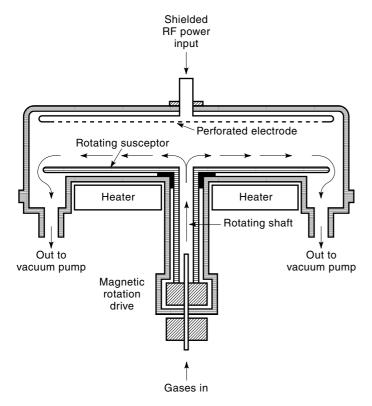


Figure 5. Modified cold-wall radial-flow, plasma-enhanced CVD reactor developed by Applied Materials had the reactants introduced from the center and exhausting from the periphery to improve the film thickness uniformity. A perforated electrode also helped create a uniform plasma (20).

within the reaction chamber. Glow discharge plasma is created selectively above each wafer, so that deposition of the dielectric films occurs only over the wafer area. Initial deposition takes place within 10 s after introducing the wafer into the chamber. The film deposit is formed in seven increments, and a finished wafer leaves the chamber typically every 50 s. Excellent uniformity of film thickness is attained. The system can be operated with dual frequency to improve film characteristics (13.56 MHz-high and 300 kHz to 400 kHz-low).

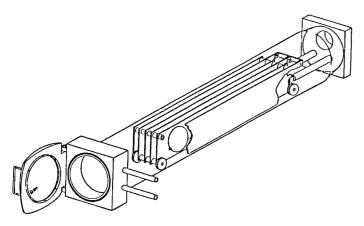


Figure 6. A schematic of a hot-wall tubular, plasma-enhanced CVD reactor introduced to increase the cassette throughput for film deposition as well as reduce contamination (20).

Operational Problems and Solutions

Most reactors are operated at conditions where the probability of homogeneous (gas phase) and heterogeneous (film forming) reactions are roughly comparable. For a parallel-plate reactor, decreasing the electrode spacing and the radical density reduces the probability of homogeneous reaction. The electrode spacing, however, cannot be arbitrarily reduced. Hence the only practical means for reducing an undesirably high level of homogeneous reactions is through lowering the radical density by reducing the electric input power or the total gas pressure (18). The properties of the end products of a plasma deposition process are generally reproducible for fixed reactor geometry operated under a fixed set of operating conditions. The optimization of these properties is largely heuristic. This makes the translating operating parameters between reactors of different construction, based on the principles of plasma chemistry, generally not possible.

The gas purity in the reactor is a function of the purity of the precursor gas, the gas delivery system, and the reactor itself. Not all impurities are equally important. Some, such as the group III and V dopants, affect the electrical behavior of amorphous silicon at ppm levels, whereas others, such as nitrogen, oxygen, and hydrocarbons, have no measurable effects (22,23) on the electrical properties at that level. Of major concern in multilayer plasma deposition processes is the so-called memory effect of gas lines and of the reactor. This memory effect is a cross-contamination phenomenon, which results from the carry-over of gaseous material and its incorporation as impurities in subsequently deposited layers. Some gases are worse than others. Diborane, fluorinated and chlorinated gases, and generally most compounds with low vapor pressure, such as ammonia and metallorganic compounds, are especially notorious in this respect. The problem is minimized by using multichamber reactors, where each chamber is dedicated to depositing a specific material, hot-walled reactors, gas lines dedicated to one gas, and procedural changes, such as sweep runs. In practice, a change of geometry potentially affects a number of important intrinsic parameters, which are not easily affected or corrected by a change in the external variables. Depletion effects, which cause ununiform film thickness and properties, may necessitate moving substrates in the gas stream to ensure the required uniformity of properties.

Film material, which accumulates on the surroundings of the deposition zone, has to be regularly removed from any deposition system to avoid the adverse effects of flakes and powder on the quality of the film deposited on the substrates. The probability that film particles dislodge from the surroundings of the reaction zone increases with time. To compound the problem, plasma deposition processes are inherently "dirty" because of the gas-phase reactions, which might occur between radicals during the deposition. Several practical solutions are used to minimize the impact of the powder and flake problem. One is to arrange the substrate surfaces vertically in the deposition chamber or horizontally above a flat counterelectrode. By this configuration, a fraction of the particulate matter generated during the process settles to the bottom of the reactor rather than on the substrate. Some designs offer a demountable counterelectrode to facilitate cleaning by mechanical or wet chemical means between runs. However, if the counterelectrodes are not removable, then the

reactor has to be etched on a regular basis by an appropriate plasma etching process. Fluorinated gases, such as CF_4 and NF_3 , are commonly used to etch amorphous silicon, silicon dioxide, and silicon nitride deposits.

Materials efficiency is defined as the ratio of the weight of the deposited film to the weight of the gas used to form the film. Defined in this way, practical reactor efficiencies rarely exceed 30%. Given the relatively low efficiency of plasma deposition processes and the high cost of the starting materials, the recycling of exhaust gases, after purification is an attractive alternative to the outright disposal of the pump effluents.

FUTURE TRENDS

The prospects for PECVD in the microelectronics industry are along two fronts: (1) development of new reactor designs to improve film quality and properties and (2) film deposition of new dielectric and oxide materials. The need to minimize or reduce radiation damage has led to the development of remote plasma-enhanced CVD reactors that independently control the generation of active species and the reaction chemistry. In this type of reactor, the plasma is confined to a region away from the substrate. This allows selective dissociation of reactants, that is, the plasma dissociates some reactants, which are then transported to the vicinity of the wafer. These active species react with other gaseous reactants that have not been exposed to the plasma, thus forming the desired film deposit. The plasma is confined by striking it in a tube on the sides of the reactor, in one end of a long reaction tube, below the substrate or above the substrate (5). In these plasma reactors, the plasma replaces the thermal energy needed to dissociate parent species by electron-molecule collisions that create a variety of radicals with near-unity reaction probability. New plasma generation techniques, such as those based on pulse dc (24), microwave (25,26) and ECR (27), are emerging for improved film deposition with reduced particle contamination and enhanced film properties. The ECR ion source creates high-density plasma by resonance of microwaves and electrons through a microwave discharge across a powerful magnetic field of 800 G to 1200 G, as shown schematically in Fig. 7 (27). This process allows film deposition at very low gas pressures (13 mPa) and at very low temperature (<275°C) and yields high rates (20).

Microwave multipolar plasmas (MMP) are 2.45 GHz glow discharges confined by multipolar magnetic fields. In MMPs, the plasma excitation and plasma–surface interactions are decoupled. There is no self-bias in MMPs and also the substrate bias and ion bombardment energies are controlled independently. Microwave excitation by distributed electron cyclotron resonance (DECR) is a technologically promising method. Magnetically enhanced plasma deposition is another configuration in which a magnet is added to confine electrons near the electrode, thereby increasing the rate of electron dissociative collisions with molecules. As a result, a glow discharge is maintained at pressures in the 0.1 Pa to 1 Pa range.

Polycrystalline silicon (polysilicon) is commercially used as the gate electrode and interconnect material in MOS integrated circuits and as the emitter material in bipolar silicon devices, the active material for thin film transistors (TFTs) and solar energy conversion devices (5). The low-pressure CVD (LPCVD) technique presently being used has two limita-

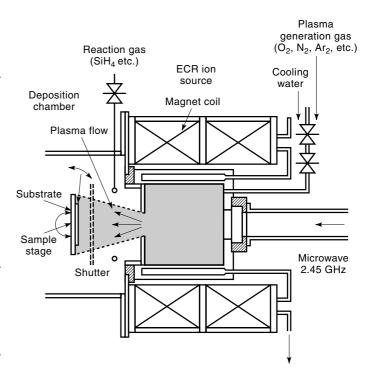


Figure 7. Schematic representation of the magnetically enhanced electron cyclotron deposition system. This configuration helps reduce the surface damage done to the wafers since the wafers are not in the direct flow of the plasma (24).

tions: (1) deposition rate and film structure are quite sensitive to deposition temperature, and (2) thickness uniformity and deposition rates are affected when relatively high concentrations of dopant species are introduced into the reactor during deposition. PECVD is being studied as an alternative to LPCVD for fabricating polysilicon gate electrodes and also as a low-temperature fabrication technique for TFTs. Silicon epitaxial layers used in silicon device technology are presently deposited by APCVD or reduced (5 kPa to 13 kPa)-pressure CVD at temperatures of 1,050°C to 1,200°C. PECVD is being considered as a promising low-temperature deposition method because of less stringent vacuum requirements and higher growth rates. PECVD also provides greater flexibility in depositing in situ doped silicon films. Silicides of molybdenum, tungsten, tantalum, and titanium have been successfully deposited by PECVD techniques. Research is focused on producing acceptable film quality.

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