Plasma deposition is a processing technique that has gained examples of devices using this technique. The third class cre-Chemical vapor deposition (CVD) has been the primary electron source and then accelerated into the plasma. The ac-

ture conditions  $(>\!\!850^{\circ}\text{C})$  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 **PLASMA DEPOSITION** cause ionization. Inductively and capacitively coupled barrel reactors and electron cyclotron resonance (ECR) reactors are popularity in the microelectronics industry in recent years be- ates and sustains the plasma by injecting large currents of cause it operates at relatively low temperatures  $\langle 250^{\circ}$ C). electrons emitted thermionically from a filament or related method of device manufacture, but high operating tempera- celerated electrons cause ionization and maintain the plasma.

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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).

density of condensable species, namely, neutral radicals and the surface and electrons enter the glow discharge. The potential relative to the gas density and the density of tial across the sheath is called the sheath pote tial across the sheath is called the sheath potential.<br>condensable neutrals is much higher than that of charged The reason for the different potentials within a plasma condensable neutrals is much higher than that of charged The reason for the different potentials within a plasma<br>narticles. Therefore, the film is predominantly formed by system becomes obvious when electron and ion mobili particles. Therefore, the film is predominantly formed by system becomes obvious when electron and ion mobilities are<br>bonding peutral radicals to the surface of the growing film considered. Imagine applying an RF field bet bonding neutral radicals to the surface of the growing film.

the plasma potential, (2) the floating potential, and (3) the first half-cycle of the field, one electrode is negative and at-<br>sheath potential. The plasma potential  $V_s$  is the potential of tracts positive ions. The othe sheath potential. The plasma potential  $V_p$  is the potential of tracts positive ions. The other electrode is positive and at-<br>the glow region of the plasma, which is normally considered tracts electrons. Because the mobil the glow region of the plasma, which is normally considered tracts electrons. Because the mobility of the electrons is con-<br>equipotential. It is the most positive potential in the chamber siderably greater than that of pos equipotential. It is the most positive potential in the chamber and is the reference potential for the glow discharge. The considering the high frequencies used in RF discharges, the floating potential  $V_f$  is the potential at which equal fluxes of flux of electrons or current is much larger than that of posinegatively and positively charged species arrive at an electri- tive ions. This situation depletes electrons in the plasma and cally floating surface in contact with the plasma. The resul- results in a positive plasma potential. On the second halftant potential is represented approximately by the following cycle, a large flux of electrons flows to the electrode that pre-

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

Because dielectric and nonconducting materials are mostly where  $T_e$  is the electron temperature, *e* is the unit electron used in the microelectronics industry. RF glow discharge is charge, and  $m_i$  and  $m_e$  are the ion charge, and  $m_i$  and  $m_s$  are the ion and electron mass, respecdiscussed more than dc glow discharge. tively (2,5,6). Most sputtering threshold energies range from 20 to 40 eV (7). Therefore it is desirable to operate the plasma **Potentials Experienced in RF Glow Discharges** with a  $(V_p - V_f)$  less than 20 eV to avoid sputtering material properties of the reactor wall, which may otherwise lead to film contam-RF glow discharges used to deposit thin films operate at fre-<br>quencies between 13.56 MHz and 50 MHz and at pressures<br>between the electrode and the glow discharge there<br>between 10 Pa to 300 Pa. The plasma density (i.e., th The degree of ionization is typically  $\langle 10^{-4}$  implying that most<br>species in the glow are neutral on the order of approximately<br> $10^{15}$  to  $10^{16}$  cm<sup>-3</sup>. High-energy electrons with energies on the<br>order of  $10^{16}$  c order of 10 to 30 eV generate the reactive species. The aver-<br>age electron energy (1 eV to 10 eV) is considerably higher<br>tial at the surface and the plasma potential determines<br>than the average ion energy (~0.04 eV) (1,5)

The potentials of glow discharges used in PECVD are (1) or electrodes positioned within a low-pressure gas. On the<br>e plasma potential, (2) the floating potential, and (3) the first half-cycle of the field, one electrode is expression (5): viously 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.

# **514 PLASMA DEPOSITION**

which is expressed as  $(3)$  action:

$$
f_c = \frac{\mu_i E_0}{\pi l} \tag{2}
$$

where  $\mu_i$  is the ion mobility,  $E_0$  is the amplitude of the ac<br>electric field, and l is the electrode spacing. The critical excita-<br>tion frequency  $f_c$  is estimated to be between 10 kHz to 100<br>kHz. below which both ion kHz, below which both ions and electrons respond to the alternating electric field. Beyond  $f_c$ , ionic species no longer re-

As electrons and molecules undergo collisions within the plasma, various excited and metastable states of species are **Film Deposition in PECVD** generated. There are two kinds of collision processes generat-<br>ing these species, elastic and inelastic collisions. Elastic colli-<br>into the following eight primary steps: sions between energetic electrons and neutral or ionized species result in little transfer of energy to the atom or ion 1. Transport of the reactants to the deposition region because of the large mass difference between the species. In- 2. Generation of condensable reactive species elastic collision processes, on the other hand, lead notably to 3. Diffusion of reactant species to the substrate surface ionization and generate species in electronically excited 4. Adsorption of the reactants onto the substrate surface<br>states. The ionization process is expressed as  $\frac{5}{2}$  Physicochomical reactions looding to the solid fi

**reaction**  $e + X \rightarrow X^+ + 2e^-$  reaction by-products

where  $X$  is a gaseous species and e is an electron. An addi-<br>tional electron is generated to contribute to maintaining the  $\frac{1}{2}$  the main gas stream tional electron is generated to contribute to maintaining the plasma. Another form of ionization termed dissociative ioniza- 8. Transport of by-products away from the desorption retion occurs, in which a molecule is dissociated and one of the gion and out of reaction chamber. atoms is ionized. This process requires a little more energy Figure 2 (9) shows a schematic of the processes involved in PECVD. The predominant flux impinging onto the substrate

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:

$$
Excitation \qquad \qquad e + X \to X^* + e^-
$$

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:

$$
\begin{aligned} \text{Excitation} &\qquad \qquad & X^* + Y \rightarrow X + Y^* \\ \text{Ionization} &\qquad \qquad & X^* + Y \rightarrow X + Y^+ + e^- \end{aligned}
$$

He and Ne, are intentionally added to plasmas to enhance from the chamber (9).

There are two distinct regions, low- and high-frequency re- the Penning process. Other types of collisional reactions are gimes in the frequency of the input power. The boundary be- dissociative attachment and dissociation. The process of distween the two regions is given by the critical frequency  $f_c$ , sociative attachment can be represented by the following re-

Dissociative Attachment

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

$$
\text{association} \qquad \qquad e + X_2 \to 2X + e^-
$$

spond as the electrons do. The relatively heavy ions do not<br>respond to the field by significant displacement and therefore<br>are considered immobile.<br>The reactive species generated in the plasma have lower en-<br>reactive speci **Example 12 Consequently react on Species** ergy barriers to physical and chemical reactions than the par-<br>
ent species and consequently react at lower temperatures.

- 
- 
- 
- 
- 5. Physicochemical reactions leading to the solid film and
- 6. Desorption of volatile by-products
- 
- 



**Figure 2.** During PECVD the reactants are transported in the gas phase to the substrate surface, a reaction generates the required mawhere *X* and *Y* are arbitrary species. Some species, such as terial to be deposited, and the byproducts are desorbed and exhausted

thin film formation process might be controlled either by the the least probable occurrence will be Eq. (d). The enthalpy of generation rate of radicals or by the surface reactions among formation  $\Delta H$  is calculated from Table 2. It is inferred that radicals. As indicated in the preceding section, various colli- the plasma decomposition of  $NH<sub>3</sub>$  occurs through the following sional processes contribute to the generation of the required primary step (3): 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

$$
Excitation \qquad \qquad e + X \to X^* + e^-
$$

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<br>rate coefficient, [X] is the concentration of species X, and [e] Similarly, radical–molecule reactions also take place (3): 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<br>inelastic collision is proportional to the probability that this<br>inelastic collision occurs and is a function of the electron en-<br>new The second is a func ergy. The rate coefficient  $k_i$  can be calculated by using the following equation (11): **Homogeneous and Heterogeneous Processes**

$$
k_i = \int_0^\infty \left(\frac{2E}{m_e}\right)^{1/2} \sigma_i(E) f(E) dE \tag{4}
$$

sights 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 summa- • Ion–surface interactions rized in Table 1 (3,12–15). The standard heats of formation 1. Neutralization and secondary electron emission of gas molecules and their fragments, shown in Table 2 (3),  $\alpha$  Sputtering of gas molecules and their fragments, shown in Table 2 (3), 2. Sputtering are useful in predicting the possible electron-impact dissocia-<br>tion reactions.<br> $\begin{array}{r} \text{Electron} \\ \text{Electron} \\ \text{Electron} \\ \text{S} \end{array}$   $\begin{array}{r} \text{S} \\ \text{S} \\ \text{S} \$ 

Electron impact dissociation of  $SiH<sub>4</sub>$  produces primary reaction products as follows: 1. Secondary electron emission

$$
SiH4 \rightarrow SiH2 + H2 \t\t ( \Delta H = 2.2 \text{ eV}) \t\t (a)
$$

$$
SiH4 \rightarrow SiH3 + H \t\t ( \Delta H = 4.0 \text{ eV}) \t\t (b)
$$

$$
SiH4 \rightarrow Si + 2H2 \qquad (\Delta H = 4.4 \text{ eV}) \qquad (c)
$$

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

surface is inferred to be radicals rather than ions, and the tion occurs. The most common primary reaction is Eq. (a) and

$$
NH3 \rightarrow NH + H2 \quad (\Delta H = 3.9 \text{ eV})
$$
 (e)  
\n
$$
NH3 \rightarrow NH2 + H \quad (\Delta H = 4.5 \text{ eV})
$$
 (f)

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

$$
\mathrm{H} + \mathrm{SiH}_4 \rightarrow \mathrm{SiH}_3 + \mathrm{H}_2 \hspace{1cm} (\Delta H = -0.5\,\mathrm{eV}) \hspace{0.5cm} (\mathrm{g})
$$

$$
H + Si2H6 \rightarrow SiH3 + SiH4 \qquad (\Delta H = -0.6 \text{ eV}) \qquad (h)
$$

$$
H+NH_3\rightarrow NH_2+N_2+H_2\quad (\Delta H=-0.04\,\mathrm{eV})\qquad (\mathrm{i})
$$

$$
SiH2 + SiH4 \rightarrow Si2H6 \quad (\Delta H = -2.1 \text{ eV}) \tag{i}
$$
  

$$
NH + NH3 \rightarrow N2H4 \quad (\Delta H = -2.4 \text{ eV}) \tag{k}
$$

In RF systems, gas-phase collisions generate condensable reactive free radicals, metastable species and ions, and thus enwhere E is the electron energy,  $m_e$  is the electron mass,  $\sigma_i$  is These reactions lead to powder formation, which is detrimentand  $f(E)$  is the electron energy distribution function that gives lead to homogeneous reactio

Heterogeneous processes result from interactions taking **Dissociation Reactions of Reactants** place between the elements in the plasma and the substrate The photolytic decomposition of a gas can provide useful in-<br>surface. Following is a summary of the primary processes of<br>sights to the most probable primary processes in the glow dis-<br>interest in plasma deposition (1):

- -
	-
	-
	-
	-
	- 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 The differences in the energy requirement for the various dis- and, particularly, ion bombardments are the most effective sociation reactions determine the ease with which each reac- methods of promoting surface reactions (16). Ions impinging

Absorption Wavelength (nm)					
Gas	Edge	Maximum	Primary Step	Secondary Step	Ref.
$\rm SiH_{4}$	150	200	$\mathrm{SiH}_2 + 2\mathrm{H}$ $SiH_3 + H$	$SiH_2 + SiH_4 \rightarrow Si_2H_6$ $H + SiH_4 \rightarrow SiH_3 + H_2$	12
$\mathrm{Si}_2\mathrm{H}_6$	210		$SiH_2 + SiH_3 + H$ $SiH_2 + SiH + 2H$ $Si2H5 + H$	$H + Si2H6 \rightarrow H2 + Si2H5$ $H + Si_2H_6 \rightarrow SiH_3 + SiH_4$	13
PH <sub>2</sub>	220	$<$ 200	$H + PH$ ,	$H + PH_3 \rightarrow PH_2 + H_2$	14
$\mathrm{B_2H_6}$	200	180	$BH3 + BH3$		14
$\mathrm{NH}_3$	210	190	$NH3 + H$ $NH + 2H$	$NH + NH_3 \rightarrow N_2H_4$	15
O <sub>2</sub>	242	140	$O + O$	$O + O_2 + M^b \rightarrow O_3 + M^b$	14
O <sub>2</sub>	300	250	$O + O2$	$Q + Q_3 \rightarrow Q_2 + 2Q$ or $2Q_2$	14
НCl	200	150	$H + Cl$	$H + HCl \rightarrow H_2 + Cl$ $Cl + Cl + M^b \rightarrow Cl_2 + M^b$	14
N,O	210	180	$N_2 + 0$	$O + N_2 O \rightarrow N_2 + O_2$ $O + N2O \rightarrow 2NO$	14
$_{\rm H_2O}$	180	165	$H_2 + O$	$O + H_2 \rightarrow OH + H$	14

Table 1. Photoprocesses of Typical Gases Used in the Production of  $Si_3N_4$ ,  $SiO_2$ , **a-Si, and BN***<sup>a</sup>*

*<sup>a</sup>* Ref. 3.

*<sup>b</sup>* M is a nonabsorbing, foreign gas.

the nature of the resulting film. Radiation damage during parameters (neutral species, ion, and electron densities; elec-PECVD displaces atoms generating vacancies, interstitials, tron energy distribution; and residence time) are controlled, dislocation loops, and stacking faults. Such damage degrades the gas-phase chemistry can be defined. Many macroscopic material properties and alters the characteristics of fabri- plasma variables (gas flow, discharge gas, pumping speed, RF cated devices. A fundamental understanding of gas-phase power, frequency, etc.) can be changed to alter the basic plasma chemistry and physics, along with surface chemistry plasma conditions. Electrode and chamber materials also almodified by radiation effects, is needed to define film-growth ter the chemistry of glow discharges because of chemical reacmechanisms. The complex interactions involved in PECVD tions on or with the surface. Synergism between these numer-

**Table 2. Standard Heat of Formation for Various Species of Gas Molecules and Their Fragments***<sup>a</sup>*

Species	Standard Heat of formation (eV)	
н	2.27	
H <sub>2</sub>	$\mathbf{0}$	
$\operatorname{Si}(g)$	4.69	
SiH	3.90	
SiH <sub>2</sub>	2.52	
SiH <sub>3</sub>	4.00	
SiH <sub>4</sub> (g)	0.32	
$\mathrm{Si}_2\mathrm{H}_6$	0.74	
N	4.92	
NH(g)	3.44	
NH <sub>2</sub> (g)	1.75	
NH <sub>3</sub> (g)	$-0.48$	
$\rm N_2H_4$	0.53	
B(g)	5.78	
ВH	4.50	
BH <sub>2</sub>	2.08	
BH <sub>3</sub> (g)	1.11	
P(g)	3.27	
PH	2.63	
$PH_3(g)$	0.06	
NO	0.94	
$N_2O$	0.85	
0	2.59	

on the surface influence the kinetics of network formation and are outlined in Fig. 3 (17). If the basic or microscopic plasma ous 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.

ous reactors are being developed to increase throughput. The



actions between the plasma parameters, kinetics of film formation, ellus (21) sequentially indexes each wafer through several deand plasma-surface interactions (17). position stations on a resistance-heated substrate plate



Figure 4. A schematic of the cold-wall radial-flow, plasma-enhanced **PECVD Reactor Systems** CVD reactor after Reinberg has the reactants introduced from the periphery of the substrate holder and exhausting in the center (19). PECVD reactors operate mostly on a batch scale, but continu-

batch reactors are (1) the radial-flow batch reactor and (2) the<br>tubular reactor. These reactors are designed to be either cold-<br>or hot-walled. In the radial-flow batch reactor, the plasma is<br>generated between two parallel ance-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  $2\%$  SiH<sub>2</sub> in N<sub>2</sub>. 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.

Figure 3. The properties of the films are controlled by complex inter-<br>A continuous-processing, radial, cold-wall reactor by Nov-



actor developed by Applied Materials had the reactants introduced from the carry-over of gaseous material and its incorporation<br>from the center and exhausting from the periphery to improve the as impurities in subsequently from the center and exhausting from the periphery to improve the film thickness uniformity. A perforated electrode also helped create a are worse than others. Diborane, fluorinated and chlorinated

ated selectively above each wafer, so that deposition of the cated to depositing a specific material, hot-walled reactors, dielectric films occurs only over the wafer area. Initial deposition as sines dedicated to one gas dielectric films occurs only over the wafer area. Initial deposi-<br>tion takes place within 10 s after introducing the wafer into<br>as sweep runs. In practice a change of geometry potentially tion takes place within 10 s after introducing the wafer into as sweep runs. In practice, a change of geometry potentially<br>the chamber. The film deposit is formed in seven increments, affects a number of important intrinsi the chamber. The film deposit is formed in seven increments, affects a number of important intrinsic parameters, which are<br>and a finished wafer leaves the chamber typically every 50 s. and easily affected or corrected by a and a finished wafer leaves the chamber typically every 50 s. not easily affected or corrected by a change in the external<br>Excellent uniformity of film thickness is attained. The system variables. Depletion effects, which Excellent uniformity of film thickness is attained. The system variables. Depletion effects, which cause ununiform film<br>can be operated with dual frequency to improve film charac-<br>thickness and properties may pecessitate m can be operated with dual frequency to improve film charac-<br>thickness and properties, may necessitate moving substrates<br>teristics (13.56 MHz-high and 300 kHz to 400 kHz-low).



reactor introduced to increase the cassette throughput for film deposition as well as reduce contamination (20). ever, if the counterelectrodes are not removable, then the

## **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 Figure 5. Modified cold-wall radial-flow, plasma-enhanced CVD re-<br>sctor developed by Applied Materials had the reactants introduced from the carry-over of gaseous material and its incorporation uniform plasma (20). 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 within the reaction chamber. Glow discharge plasma is cre-<br>ated selectively above each wafer, so that deposition of the cated to depositing a specific material hot-walled reactors 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 de-**Figure 6.** A schematic of a hot-wall tubular, plasma-enhanced CVD signs offer a demountable counterelectrode to facilitate clean-<br>reactor introduced to increase the cassette throughput for film deposition ing by mechanica

reactor has to be etched on a regular basis by an appropriate plasma etching process. Fluorinated gases, such as  $CF_4$  and NF3, 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,<br>which are then transported to the vicinity of the wafer. These<br>active species react with other gaseous reactants that have<br>not been exposed to the plasma, thus for 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 reac- tions: (1) deposition rate and film structure are quite sensitive tors, the plasma replaces the thermal energy needed to disso- to deposition temperature, and (2) thickness uniformity and ciate parent species by electron–molecule collisions that cre- deposition rates are affected when relatively high concentraate a variety of radicals with near-unity reaction probability. tions of dopant species are introduced into the reactor during New plasma generation techniques, such as those based on deposition. PECVD is being studied as an alternative to pulse dc (24), microwave (25,26) and ECR (27), are emerging LPCVD for fabricating polysilicon gate electrodes and also as for improved film deposition with reduced particle contamina- a low-temperature fabrication technique for TFTs. Silicon epition and enhanced film properties. The ECR ion source cre- taxial layers used in silicon device technology are presently ates high-density plasma by resonance of microwaves and deposited by APCVD or reduced (5 kPa to 13 kPa)-pressure electrons through a microwave discharge across a powerful CVD at temperatures of  $1,050^{\circ}$ C to  $1,200^{\circ}$ C. PECVD is being magnetic field of 800 G to 1200 G, as shown schematically in considered as a promising low-temperature deposition Fig. 7 (27). This process allows film deposition at very low gas method because of less stringent vacuum requirements and pressures (13 mPa) and at very low temperature  $\langle 275^{\circ}$ C) higher growth rates. PECVD also provides greater flexibility and yields high rates (20). in depositing in situ doped silicon films. Silicides of molybde-

discharges confined by multipolar magnetic fields. In MMPs, fully deposited by PECVD techniques. Research is focused on the plasma excitation and plasma–surface interactions are producing acceptable film quality. decoupled. There is no self-bias in MMPs and also the substrate bias and ion bombardment energies are controlled in- **BIBLIOGRAPHY** dependently. Microwave excitation by distributed electron cyclotron resonance (DECR) is a technologically promising<br>method. Magnetically enhanced plasma deposition is another<br>configuration in which a magnet is added to confine electrons<br>mear the electrode, thereby increasing the ra

grated circuits and as the emitter material in bipolar silicon  $pp. 21-43$ . devices, the active material for thin film transistors (TFTs) 4. S. M. Rossnagel, Glow discharge plasmas and sources for etching and solar energy conversion devices (5). The low-pressure and deposition, in J. L. Vossen and W. Kern (eds.), *Thin Film* CVD (LPCVD) technique presently being used has two limita- *Processes II,* San Diego: Academic Press, 1991, pp. 11–77.



Microwave multipolar plasmas (MMP) are 2.45 GHz glow num, tungsten, tantalum, and titanium have been success-

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- sociative collisions with molecules. As a result, a glow dis-<br>charge is maintained at pressures in the 0.1 Pa to 1 Pa range.<br>Polycrystalline silicon (polysilicon) is commercially used as<br>the gate electrode and interconnect
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### **520 PLASMA IMPLANTATION**

- 5. R. Reif, Plasma-enhanced chemical vapor deposition, in J. L. Vos- *and Techniques,* Park Ridge, NJ: Noyes Publications, 1988, pp. sen and W. Kern (eds.), *Thin Film Processes II,* San Diego: Aca- 112–146. demic Press, 1991, pp. 525–564.
- 6. J. L. Vossen, Glow discharge phenomena in plasma etching and ALBERT A. ADJAOTTOR plasma deposition, *J. Electrochem. Soc.*, 126: 319, 1979. **EXECTATHIOS I. MELETIS**
- 7. A. Sherman, Plasma-assisted chemical vapor deposition pro- Louisiana State University cesses and their semiconductor applications, *Thin Solid Films,* **113**: 135, 1984.
- 8. M. Rand, Plasma-promoted deposition of thin inorganic films, *J. Vac. Sci. Technol.,* **16**: 420–427, 1979.
- 9. M. J. Hampden-Smith and T. T. Kodas, Chemical vapor deposi-<br>tion of metals: Part 1. An overview of CVD processes, *Chem. Va-*<br>MENTATION. por Deposition, **1** (1): 8-23, 1995.
- 10. H. Y. Kumagai, in McD. Robinson et al. (eds.), *Proc. 9th Int. Conf. Chem. Vapor Deposition,* Pennington, NJ: Electrochemical Society, Vol. 84-6, 189, 1984.
- 11. G. Turban, Y. Catherine, and B. Grolleau, Reaction mechanisms of radio frequency glow discharge deposition process in silanehelium, *Thin Solid Films,* **60**: 147–155, 1979.
- 12. G. C. A. Perkins and F. W. Lampe, *J. Amer. Chem. Soc.,* **102**: 3764, 1980.
- 13. T. L. Pollock et al., Photochemistry of silicon compounds. IV Mercury photosensitization of disilane, *J. Amer. Chem. Soc.,* **95**: 1017, 1973.
- 14. H. Okabe, *Photochemistry of Small Molecules,* New York: Wiley Interscience, 1978.
- 15. J. R. MacDonald, V. M. Donnelly, and A. P. Baronauski, ArF laser photodissociation of  $NH<sub>3</sub>$  at 193 nm: Internal energy distribution of  $\mathrm{NH}_2\mathrm{X}^2\mathrm{B}_1$  and  $\mathrm{A}^2\mathrm{A}_1$ , and two photon generation of  $\mathrm{NH}\; \mathrm{A}^3\Pi$ and  $\beta^1\Sigma^+$ , *Chem. Phys.*, **43**: 271, 1979.
- 16. U. Gerlach-Meyer, J. W. Coburn, and E. Kay, Ion-enhanced gassurface chemistry: The influence of the mass of the incident ion, *Surf. Sci.,* **103**: 177–188, 1981.
- 17. Y. Catherine, in G. S. Mathad, G. C. Schwartz, and G. Smolinsky (eds.), *Plasma Processing,* Pennington, NJ: Electrochemical Society, 1985, p. 317.
- 18. F. Jansen, Plasma deposition processes, in J. Mort and F. Jansen (eds.), *Plasma Deposited Thin Films,* Boca Raton, FL: CRC Press, 1986, pp. 1–19.
- 19. W. C. Dautremont-Smith, R. A. Gottscho, and R. J. Schutz, Plasma processing: Mechanisms and applications, in G. E. McGuire (ed.), *Semiconductor Materials and Process Technology Handbook,* Park Ridge, NJ: Noyes Publications, 1988, p. 191.
- 20. A. Sherman, *Chemical Vapor Deposition for Microelectronics,* Park Ridge, NJ: Noyes Publications, 1987, Chaps. 2 and 5.
- 21. E. R. van de Ven, I.-W. Connick, and A. S. Harrus, *Proc. 7th Int. IEEE Multi-Level Interconnection Conf.,* Santa Clara, CA, 194, June 1990.
- 22. C. C. Tsai, J. C. Knights, and M. J. Thompson, "Clean" a-Si: H prepared in a UHV system, *J. Non-Cryst. Solids,* **66**: 45, 1984.
- 23. R. W. Griffith et al., Modifications in optoelectric behavior of plasma-deposited amorphous semiconductor alloys via impurity incorporation, *J. Non-Cryst. Solids,* **35–36**: 391, 1980.
- 24. K. S. Mogensen et al., Optical emission spectroscopy on pulsed dc plasmas used for TiN deposition, *Surf. Coat. Technol.,* **102** (1–2): 41–49, 1998.
- 25. F. Galluzzi et al., CVD diamond films as photon detectors, *Nuclear Instr. Meth. Phys. Res., Section A,* **409** (1–3): 423–425, 1997.
- 26. T. Osamu and H. Tomofumi, Microwave plasma-enhanced CVD for high rate coating of silicon oxide, *Trans. Inst. Metal Finish.,* **76** Part 1: 16–18, 1998.
- 27. V. S. Nguyen, Plasma-assisted chemical vapor deposition, in K. K. Schuegraf (ed.), *Handbook of Thin-Film Deposition Processes*