CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) coating methods were developed from techniques employed as early as 1880 by the incandescent lamp industry. Early applications included the deposition of pyrolytic carbon and metals, in an attempt to improve on the fragile filaments then in use. From 1909 to 1939, various halide-reduction and halide-decomposition processes were used to prepare tantalum, titanium, zirconium, and other refractory metals. The development of vapor deposition as a means of applying protective coatings took place largely after 1935. Silicon was first deposited by hydrogen reduction of silicon tetrachloride. Silicon gained importance with the preparation of silicon-based photocells and rectifiers and has an ever-increasing importance to our present electronics technology.

The technological importance of CVD cannot be overstated. Remarkably versatile in the range of possible materials and structures, CVD is used in virtually all fields of manufacturing and technology. Applications of CVD span many important industries from metallurgical applications to hard coatings for wear resistance and corrosion protection of special tools. Morphology, lateral and vertical growth rates, composition, stress, uniformity, and electrical and optical properties can all be modified and controlled through alterations in the chemistry and reactor conditions. A large variety of crystalline and amorphous elements and compounds, in bulk form, as coatings and thin films, can be synthesized by this method, usually at a relatively low temperature and with a high degree of purity and controlled microstructure. The use of CVD has grown considerably in the preparation of high-purity metals, various coatings, and electronic materials in the past 50 years or so. In semiconductor technology, CVD plays the central role in the formation of electronic and optical devices. CVD of polycrystalline and amorphous materials is equally important—for example, in dielectrics for the electronics industry. CVD provides lateral control of growth, not possible with other deposition methods, as well as the capability for integrated processing of semiconductors with dielectrics such as oxides and nitrides. Without a doubt, the stringent requirements and demands of the semiconductor and microelectronic industries have fueled the development of CVD techniques and the efforts for the understanding of the basics of CVD processes. CVD, along with its variations, is the workhorse of the semiconductor industry, and the existence of this industry in the present form would be impossible without it.

A large body of literature and reviews now exists on CVD. Since 1980 the CVD literature has grown exponentially. Vossen and Kern (1) and Hess and Jensen (2) have given comprehensive reviews of CVD and CVD technology, particularly in the semiconductor industry.

The CVD process is used in almost every step of the electronics manufacturing process. Thin films of metals, dielectrics, and semiconductors are being deposited in a variety of physical states with a control that extends to the nanometer scale in deposition thickness. Since its rather empirical beginnings, our understanding of the CVD process has grown tremendously. The complex mass transport, fluid mechanics, and chemical behavior of these systems can be modeled with some accuracy. These models have allowed the design and optimization of the CVD reactor and process enabling the development of large-diameter single-wafer machines as well as high-capacity multiwafer systems. The diversity of reactors, chemical systems, and operating conditions used in the CVD technology has allowed this technology to flourish and command a greater role in the electronic manufacturing process.

THE CVD PROCESS

In chemical vapor deposition, as the name indicates, chemically reacting gases are used to synthesize a thin solid film. In the broadest sense, it includes techniques to deposit epitaxial, polycrystalline, and amorphous films. These techniques also can vary substantially in their physical embodiment. Plasma-enhanced CVD (PECVD), photoassisted CVD, thermally driven CVD, and a large number of variations are used to take advantage of specific chemical reactions in order to deposit a thin film of a given structure and composition. Also, the same physical concepts are involved in etching, a widely used process in which a thin layer of material is removed from the wafer. The specific variations mentioned above are covered elsewhere in this encyclopedia. The focus of this article is the fundamental processes in CVD and its applications in the microelectronic industry.

In a typical CVD process, the reactants in gaseous form are often diluted in a carrier gas such as hydrogen or nitrogen, and they subsequently flow continuously through a reactor and over a suitable hot surface (wafer) called a substrate, onto which the solid film is deposited. Chemical reactions take place in a hot zone of the chamber and on the heated substrate, leading to a growth of the thin film. Homogeneous gas-phase as well as heterogeneous surface reactions may be involved in the film growth. The CVD process, with its numerous gas-phase reactions and complex flow field, compares well

J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*. Copyright © 1999 John Wiley & Sons, Inc.

with the combustion process; and its surface reactions have similarities with the heterogeneous catalysis. The inclusion of a gas compound containing a dopant species permits the in situ incorporation of that impurity in the deposited film, the level of which is easily controlled by monitoring the partial pressure of this gas compound and the specification of the operating conditions of the reactor.

The basic process steps are illustrated schematically in Fig. 1. Each of these steps is a complex phenomenon and directly affects the film characteristics. It is necessary to understand and be able to control them. The seven major steps are as follows:

1. Transport in the bulk gas phase (convection, diffusion and heat transport)
2. Gas-phase reactions
3. Diffusion of gaseous species to the growth surface
4. Adsorption on the surface
5. Surface diffusion of precursors and reactions
6. Nucleation and incorporation of surface species into the film
7. Desorption of volatile species

In a majority of cases, what happens in the bulk gas phase, such as transport and gas-phase chemistry, is very well studied and documented. The lack of knowledge of the chemical and transport processes on the growth surface is a present major challenge in the development of a complete understanding of the CVD process. Fortunately, this knowledge gap is being filled, albeit slowly.

The technological application of CVD also demands that the final product possess reproducible and controllable properties like composition, thickness, uniformity, and surface morphology. Many of these manufacturing-based issues can be addressed without the complete atomistic physical and chemical model of the growth process.

CVD Reactor Systems

A variety of CVD reactor designs are used in practice with the design dictated by constraints due to the chemistry employed, wafer throughput, and materials uniformity. The reactor geometry and the gas flow distribution technique along with the operating conditions within the system, such as the reactant gas partial pressure, the total pressure in the chamber, wafer temperature, and reactor wall temperature, can affect the resulting film deposition rate. The essential design schematic is shown in Fig. 2, and it consists of a gas-handling system, a reactor, a system to supply heat, an exhaust section, and an appropriate pumping system.

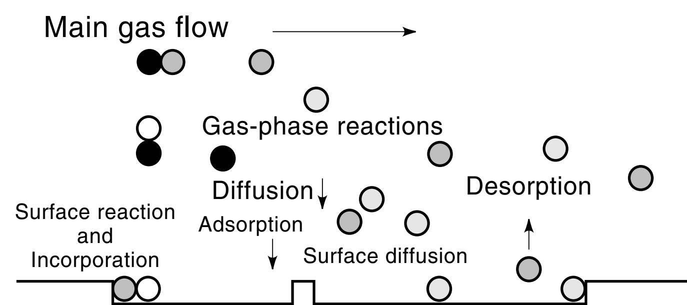


Figure 1. Schematic of elementary processes involved in the chemical vapor deposition process.

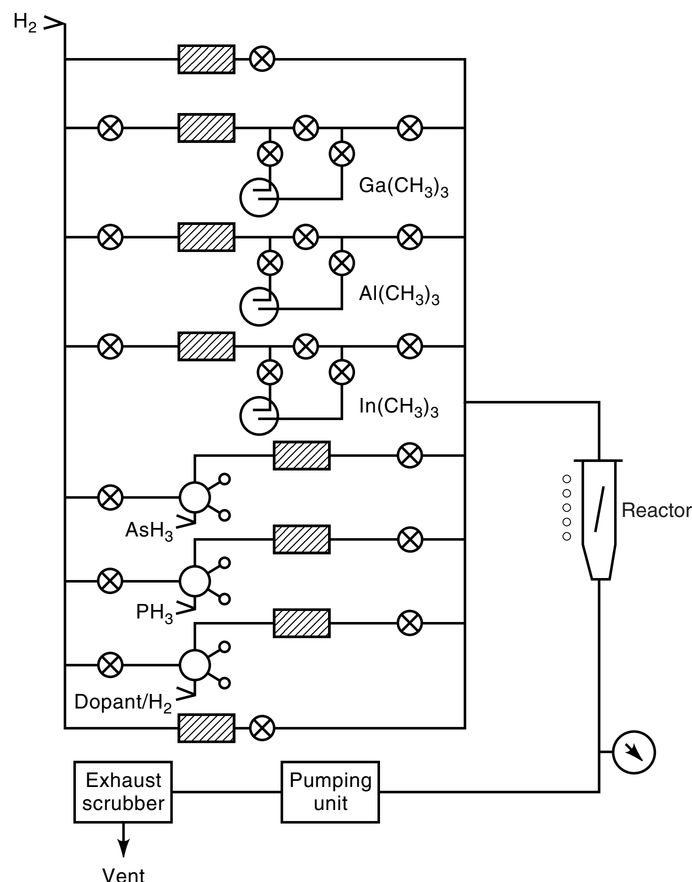


Figure 2. A typical CVD system is composed of a gas panel (used for mixing and feeding the gas into the reactor), a reactor vessel, and a suitable system for controlling the reactor pressure and handling the reactor effluent. The reactor may be heated by lamps, by radio-frequency (RF) induction heating, or by placement into a tube furnace. (Reprinted from *Materials Science and Engineering Reports,* Vol. 2, T. F. Kuech, Metal Organic Vapor Phase Epitaxy of Compound Semiconductors, p. 6, 1987, with permission from Elsevier Science Publishers.)

The function of the gas-handling system is to deliver a precisely metered gas mixture to the reactor from the liquid and gas sources. Care has to be taken to ensure a leak-free system with no recondensation of the sources in gas lines. Liquids, when used as sources, are normally used in bubblers kept at a constant temperature bath. An inert gas bubbled through the liquid source is saturated with its vapors which then can be transported with ease to the reactor.

Reactor Types

Because of the numerous applications of CVD, there are a variety of reactor configurations in use. The most common ones are shown in Fig. 3. Reaction chambers can be broadly classified into horizontal and vertical reactors. These designs have also been the focus of most modeling efforts. Each of these could be a hot-walled or a cold-walled reactor. In cold-walled reactors the steep thermal gradients over the heated

substrate can lead to the formation of complex buoyancy-driven recirculation flows. Several design modifications have been devised to reduce or eliminate these undesirable return flows, such as low pressure and high linear gas velocities within the reactor.

In a vertical configuration, reactants are normally introduced from the top. Common variations in the basic design include substrate rotation, downward facing substrates with inverted stagnation point flow, and the "chimney" reactor. In the last two configurations, the overall gas flow is from bottom to top. The alignment of the natural and forced convection reduces the possibility of circulation in the reactor.

A special type of vertical reactor is the barrel reactor. It is designed to be a high-throughput reactor, with commercial systems accommodating five to 20 wafers. Though it is one of the primary tools used in Si epitaxy, small barrels are being used in GaAs technology. Pancake reactors are another multiwafer commercial system. The multiwafer reactors are often difficult to optimize for growth and compositional uniformity due to complex flow behavior and the need for uniform heating.

The horizontal reactor, with its simple design and ability to accommodate multiple wafers, is the mainstay for the production of polycrystalline silicon, dielectrics, and passivation films. One common variation, but with limited wafer capacity, has the susceptor tilted into the gas stream to improve thickness uniformity of the films. Variations of the horizontal reactors also include substrate rotation, inverted substrate, single-wafer and multiwafer rotating disk reactors, and multiwafer planetary motion reactors.

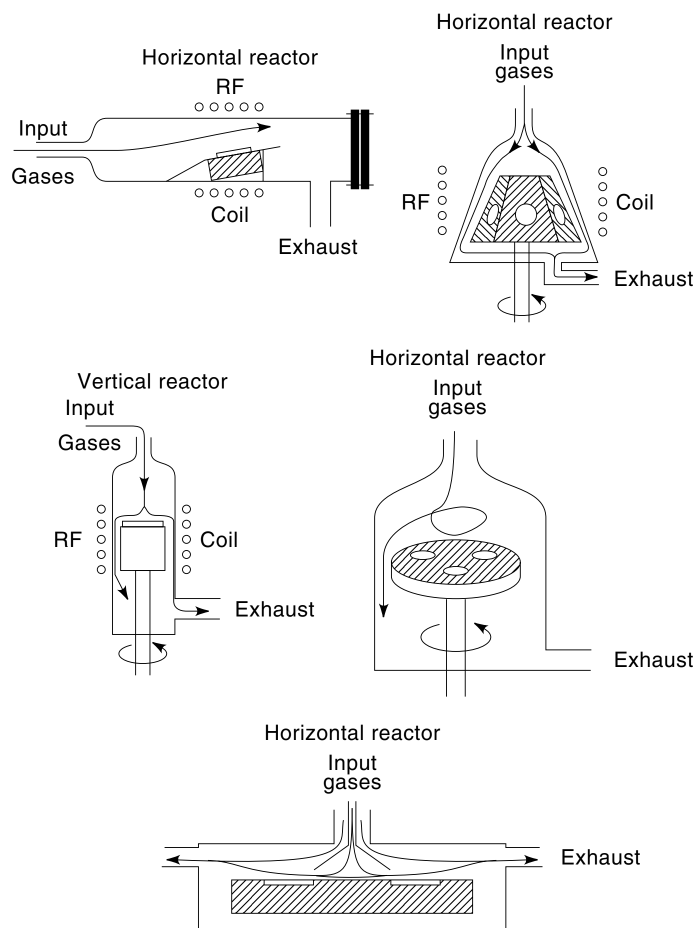


Figure 3. There are several reactor designs that are common in the literature and in practice. These varying designs reflect the diversity of uses because CVD is a dominant thin film deposition technique. [Reproduced from *Thin Film Processes II,* J. L. Vossen and W. Kern (eds.), Chapt. III-2, 1991, by permission of Academic Press.]

CVD TECHNIQUES

A convenient classification of the CVD process is based on (1) the pressure regime used in the reactor and (2) the source of energy employed to drive the chemical reactions leading to deposition. Low-pressure CVD (LPCVD) and atmospheric-pressure (APCVD) systems are used in a variety of deposition applications. The higher-pressure systems typically allow for higher growth rates and a simplified gas-handling system. An array of energy sources have been used for CVD applications, including thermal CVD, plasma CVD, and photoenhanced CVD, referring to the specific method of energy input to the chamber and the wafer.

Thermal CVD. In thermal CVD within a hot-walled reactor, heat is supplied by placing the reactor inside an oven or a furnace. In cold-wall configurations, the wafer and holder is heated by the resistive or inductive heating of a graphite (or other conducting) substrate. The direct heating of the wafer and carrier leads to low heating of the reactor walls. Radiative heating can also be carried out using high-wattage lamps and high-power lasers directed onto the wafer itself.

Temperature control in cold-walled reactors can be quite difficult. In order to get a high degree of uniformity over the wafer surface, the reactor is often operated under mass-transport-controlled conditions. In these cases, the surface processes are much faster than the gas-phase transport, and consequently the growth rate is limited by the diffusive transport of gas-phase nutrients from the gas phase to the surface where they are rapidly consumed. Film uniformity can often be improved under a kinetically controlled regime. Kinetically limited film growth occurs when the gas-phase transport processes are fast compared with the surface reactions leading to film deposition. A precisely controlled and uniform wafer temperature is required and can be more easily achieved in hot-walled reactors. A disadvantage of the hot-walled reactor is the subsequent coating of the reactor wall with the growth product since any heated surface will serve as a suitable reaction site. Depending on which of the subprocesses determines the rate of the thermal CVD reaction, the films produced can be extremely conformal to the substrate topography. A new trend in thermal CVD is a process called rapid thermal CVD (RTCVD), wherein rapid temperature cycling is employed in a single-wafer configuration. This reactor type limits the time at temperature experienced by a wafer in applications where the thermal history is important to the final device structure.

Plasma-Enhanced CVD (PECVD). The chief function of high temperatures is to stimulate gas-phase and surface reactions by producing activated species and radicals. Generation of plasma accomplishes the task, but at considerably lower temperatures. Some heating is still needed for many CVD pro-

cesses, but these temperatures can be several hundred degrees lower than in conventional thermal CVD. The reduced temperatures of plasma CVD can be attractive where the thermal history of the wafer is important. With the decreasing size of devices used by the silicon technology industry, this method is becoming increasingly important.

Since plasma is a complex mixture of activated species, radicals, ions, and electrons, process characterization is quite complicated. PECVD is sensitive to system variables such as gas pressure, flow rate, RF power and frequency, reactor geometry, and substrate temperature in an often complex manner. The energetic particles like positive ions, metastable species, and electrons striking the surface profoundly affect the surface chemistry through inducing chemical reactions as well as through direct impact with adsorbed species in the growth surface. The highly energetic positive ions and electrons can also degrade the film morphology through the ion-based or sputter erosion of the surface. To alleviate this problem a reactor configuration devised called remote PECVD (RPECVD) generates plasma away from the surface and energetic thermalized species diffusive to the growth surface, allowing only the lower-energy molecular and atomic species to reach the surface.

PECVD is covered in detail elsewhere in this encyclopedia.

Photoenhanced CVD. Electromagnetic radiation, of suitable frequency, can interact with gas or surface species; and absorption of this energy quanta, along with the pyrolysis of impinging gas-phase species on the substrate, can initiate chemical reactions. Photoassisted or photoenhanced CVD, using laser light as well as ultraviolet light from lamps, can significantly lower deposition temperatures, when compared with thermal CVD, and reduces the ion-induced damage to the deposited film often experienced in PECVD. Other major advantages are the possibility of localized deposition through the focusing of the radiative energy onto the surface, minimizing unwanted reactions by tuning the frequency of incident radiation, and maintaining a small well-defined reaction volume. The potential advantages of low temperature and selected area growth makes this a fertile area of research. Plasma-based processing is discussed in detail elsewhere in this encyclopedia.

Fundamental Processes in Thermal CVD

The CVD process is generally divided into the three fundamental processes: gas-phase chemistry, surface chemistry, and transport phenomena. The chemical mechanisms underlying a CVD process are complex, involving both gas-phase and surface reactions. Gas-phase reactions decrease in importance with reduced temperature and reactant partial pressure. At very low pressures, only the surface reactions may be of importance simplifying the overall chemical nature of the CVD system. The relative importance of fluid flow, convective heat transfer, and radiative heat transfer is determined by the operating conditions and the chamber geometry.

Transport Phenomena. Fluid mechanics plays a major role in CVD since the specific flow conditions determine diffusive and convective mass transport and the temperature fields in the reactor. The factors influencing these properties are those that govern the velocity, temperature, and concentration gradients that develop in the reactor. These flow fields and the associated wide variety of flow structures, in turn, depend on the reactor geometry, inlet and exhaust manifolds, type of carrier gas, flow rate, and operating pressure and temperature. The flow in most CVD reactors is laminar. Velocities approaching turbulent flow are rarely encountered and may be present in large-diameter multiple wafer rotating disk reactors. The reactor geometry may present some obstacles disturbing the flow pattern from the ideal laminar flow, resulting in eddies and vortices. These complex flow patterns lead to the reintroduction of reaction byproducts into the inlet gas stream. This time-dependent change in the gas feed to the reactor can result in the generation of particulates and a degradation of the film properties.

For flows other than the free molecular flow type, the major forces normally encountered in a typical CVD reactor are inertial forces, viscous forces, and a gravity-derived buoyancy force. The flow types are classified into different flow regimes depending on the pressure and system dimensions.

FLOW REGIMES

CVD reactors are sometimes conveniently classified depending on the operating pressure: low-pressure CVD (LPCVD), atmospheric-pressure CVD (APCVD), subatmospheric CVD (SACVD), and ultra-low-pressure CVD (ULPCVD). Jensen (3) discusses the transport phenomena encountered in a variety of these systems.

Molecular Flow

Pressure controls the mean free path of the molecules. A dimensionless parameter, called Knudsen number, is defined as $Kn = l/a$, where a is a characteristic dimension of the reactor and l is the mean free path. When Knudsen number is less than 0.01, the mean free path is very small compared with the characteristic dimensions of the flow. Such a flow is adequately described by continuum fluid mechanics. On the other hand, for Knudsen numbers greater than 10, gas-wall collisions become important and the flow is molecular in nature. In the case of molecular flow, the description of the flow fields or patterns within the reactor using continuum mechanics turns out to be inadequate, and a description based on a statistic mechanical approach using kinetic theory must be invoked. In transition flow regime at an intermediate range of Knudsen numbers, both the gas–gas and gas–wall collisions are important. An accurate description of the flow behavior in this transitional regime is difficult to treat mathematically. In a given system, the flow regime depends on the focus of investigation. For example, in a typical LPCVD reactor operating at 0.1 torr, the Knudsen number is well below 0.01, allowing the use of continuum fluid mechanics to describe the flow behavior. Within the system at the wafer surface, however, the deposition of material over or into a topological feature such as a groove or trench in the surface may require the use of a molecular flow description. For example, if a 0.5 μm trench is being filled by a CVD deposit, the characteristic dimension of the flow changes from the reactor diameter to that of the width of the trench and the Knudsen number now is well above 1000. The prediction or modeling of these processes can therefore span a broad spectrum of length scale

which demands a change in the physical description of the mass transport to and over the surface.

Laminar Flow

In a typical LPCVD reactor, the high gas velocities typically employed lead to the presence of laminar flow behavior where there are no recirculations within the reactor. Reynolds number, Re, is the ratio of inertial to viscous forces and characterizes this flow regime:

$$\mathrm{Re} = \frac{DV\rho}{v}$$

where ρ is the density of the gas, V is the linear velocity, D is the characteristic dimension of the reactor, and v is the dynamic viscosity. Low Reynolds numbers imply relatively stable laminar flow.

Isothermal flows with a Reynolds number below 2100 are considered to be laminar. An increase in temperature reduces the Reynolds number and further stabilizes the flow. Under these conditions, viscous forces dominate, leading to a simple parabolic (or near parabolic, in the case of a nonisothermal system) velocity profile in a developed flow, with the gas velocity being zero at the walls and reaching a maximum in midstream. When the gas enters the reaction chamber through the inlet nozzle, it has to adjust to the new dimensions; but before it can do so, there is chaotic activity near the entrance, and inertial forces dominate. The gas, as soon as it comes in contact with the chamber wall, decelerates because of viscous forces and there is a very thin layer near the wall in which the velocity is considerably smaller and laminar than at a larger distance from it. This region in the gas stream adjacent to the surface is called the boundary layer, the thickness of which increases along the wall in a downstream direction and can eventually occupy the entire reactor cross section. The full development of the laminar flow profile in the reactor requires that this boundary layer grow across the reactor diameter. This development requires a certain length of reactor that depends on the gas properties, pressure, velocity, and composition. The provision required for a well-developed and stable fluid flow behavior is a critical design consideration for many reactor designs.

MIXED CONVECTION PHENOMENA

The superimposition of buoyancy-driven flows due to gas-phase density gradients, resulting from temperature gradients as well as compositional variations on the forced flow entering the reactor leads to a mixed convection type of flow. Mixed convection is encountered in reduced atmospheric pressure (0.1 atm to 1 atm) systems, and it is severe in reactors where the overall flow direction is not from bottom to top.

In horizontal reactors, the buoyancy forces are perpendicular to the general flow direction. The coexistence of natural or gravity-based and forced convection leads to two types of recirculation: (1) transverse recirculations whose axis of rotation is horizontal and perpendicular to the direction of bulk flow and (2) longitudinal recirculations that produce a helical motion of the fluid in the downstream direction and has its axis of rotation parallel to the direction of bulk flow. The rotation direction of the transverse recirculations depends on whether the walls of the reactor are insulated or cold and on the inlet conditions. These types of flow behavior have been described in a large number of publications. A temperature gradient between the top and the bottom, beyond a certain critical point, leads to flow instabilities and the presence of recirculation cells. Various experimental and flow visualization studies indicate the presence of one or more recirculation cells and the existence of complex time periodic "snaking" motion and chaotic flows when transverse recirculations coexisted with the longitudinal recirculations.

In the vertical reactor, the feed gas is typically introduced at the top while the inlet gas stream impinges on the deposition surface, which may be rotating resulting in the fundamental axisymmetric flow type of the so called stagnation point flow. Von Karman similarity solution provides the basis for its analysis (4). The temperature gradient due to the heated surfaces can result in unstable density gradients, which generate two- and three-dimensional thermal convection flows superimposed on the forced reactor flow. Many researchers have made important contributions in understanding this phenomenon and in identification of operating conditions leading to stable flows and uniform growth despite these complicating factors. Such computational and experimental studies have found that a key parameter governing the performance in vertical reactors is the reactor design, which can be optimized to eliminate flow separations and to minimize the formation of recirculation cells because of forced convection. The internal distance between the gas inlet and the heated susceptor governs the strength of natural convection and hence the onset of buoyancy-driven recirculations. If the substrate holder or susceptor is rotated, this rotation can create a uniform thin boundary layer resulting in uniform deposition rate, and the stronger pumping action helps reduce the effect of natural convection.

The performance of all these CVD systems depends on the details of the reactor design and operating conditions. The internal temperature gradients, pressure (density), velocity, reactor geometry, and physical properties of the gases all affect the flow structure, its stability, and its temperature distribution. The temperature distribution, in turn, strongly affects reaction rates. The operating pressure is also important since it strongly affects the flow structure, where low pressure effectively eliminates recirculations, the gas-phase diffusivity, and hence mass transport, and again low pressure increases diffusivity and in general makes the growth rate more uniform. Finally, many gas-phase reactions strongly depend on pressure and the residence time, with the reaction rates decreasing with decreasing reactor pressure.

CVD CHEMISTRY

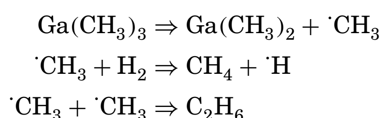
Chemistry is the next important element in the description and analysis of any CVD reactor. Both the gas-phase reactions and transport as well as the surface phenomena are important. The gas-phase mechanisms are well established for the most common cases encountered in the semiconductor industry. The lack of information of the surface processes hampers the development of a complete understanding of the CVD process at present.

A CVD process is a nonequilibrium chemical system. Though not directly applicable to film growth, the study of

most chemical systems starts with an equilibrium thermodynamic analysis of the overall process. Tirtowidjojo and Pollard (5) and Coltrin et al. (6) present such analyses for the CVD-based growth of GaAs and Si, respectively. This analysis provides important information about the feasibility of reaction pathways and expected maximum extent of a particular reaction. The free energy change, stimulated by some appropriate energy source, provides the driving force for the reactions. The thermodynamic analysis of chemical systems is treated in many physical chemistry texts (7).

Kinetic Mechanisms

Gas-Phase Reactions. Thermodynamic analysis underscores the feasibility of a particular reaction. For example, the formation of Si from SiH_4 is favored by the reduction in free energy and may lead to the conclusion that SiH_4 will spontaneously decompose (under most conditions) to Si and H_2. SiH_4 is, however, stable at room temperature and higher. In order for the reaction to proceed forward, the reactants have to overcome the energy barrier preventing spontaneous decomposition achieved by introduction of energy, in thermal or other forms. There are a wide variety of gas-phase reactions leading to the eventual deposition of the thin film. The initial decomposition reaction could yield very reactive and unstable species (such as free radicals) which can further react with the gas-phase constituents to yield a number of intermediate species. One such group of intermediates is free radicals that then react with other molecules and free radicals, abstracting atoms or simply combining with them. These reactions form an important set of reactions occurring in a CVD system. The methyl and dimethyl gallium radicals formed as a result of homogeneous decomposition of trimethyl gallium may take part in further reactions as shown below.

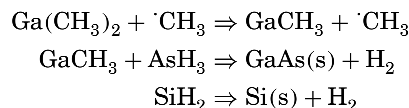


$$Ga(CH_3)_3 \Rightarrow Ga(CH_3)_2 + {}^{\cdot}CH_3$$
$${}^{\cdot}CH_3 + H_2 \Rightarrow CH_4 + {}^{\cdot}H$$
$${}^{\cdot}CH_3 + {}^{\cdot}CH_3 \Rightarrow C_2H_6$$

Some large organic molecules with a branched structure may also undergo internal rearrangement and in the process eliminate a fragment radical. β-hydrogen elimination is one such reaction. For example, triethyl gallium may undergo β-hydrogen elimination reaction leading to other stable, nonradical species that participate in the growth reaction: $Ga(C_2H_5)_3 \Rightarrow GaH(C_2H_5)_2 + C_2H_4$.

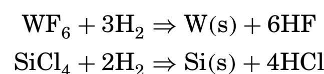
These kinetic steps can and do occur in the gas phase and at surfaces. The slowest of these steps will determine the characteristic temperature and pressure dependence of the overall growth process. The following reaction types are typically encountered in the CVD systems.

Pyrolysis. Film deposition in many CVD systems is made possible by pyrolytic or thermal decomposition of the gaseous reactants near or at the wafer surface. The first step in these processes is the generation of active chemical species in a series of reactions leading to the final product. Hydrides, metal hydrides, organometallic compounds, and other heavy, long-chained and branched compounds are particularly suitable starting materials. Such reactive, intermediate species such as $Ga(CH_3)_3 \Rightarrow Ga(CH_3)_2 + {}^{\cdot}CH_3$ and $SiH_4 \Rightarrow SiH_2 + H_2$ then further react or decompose to yield the desired product:



$$Ga(CH_3)_2 + {}^{\cdot}CH_3 \Rightarrow GaCH_3 + {}^{\cdot}CH_3$$
$$GaCH_3 + AsH_3 \Rightarrow GaAs(s) + H_2$$
$$SiH_2 \Rightarrow Si(s) + H_2$$

Reduction. Hydrogen is often used in CVD systems, serving as both (1) a carrier gas diluting the reactants and (2) an active chemical component as a reducing agent. Hydrogen reduction is used in the deposition of many compounds. Common examples include reduction of tungsten hexafluoride and silicon tetrachloride, leading to tungsten metal and Si deposition, respectively:



$$WF_6 + 3H_2 \Rightarrow W(s) + 6HF$$
$$SiCl_4 + 2H_2 \Rightarrow Si(s) + 4HCl$$

Oxidation and Nitridation. There are a variety of oxidizing agents used in the CVD deposition of insulating or other oxide films. Silicon dioxide, SiO_2, is a common insulator in the microelectronics industry. Oxygen, water, and nitrous oxides are commonly used due to the ease in handling. For example, SiO_2 can be deposited from silane in the presence of oxygen through the reaction $SiH_4 + 2O_2 \Rightarrow SiO_2 + 2H_2O$. Ammonia, NH_3, is also used in the deposition of nitride films. The most common example is the formation of silicon nitride films by ammonolysis of silane: $3SiH_4 + 4NH_3 \Rightarrow Si_3N_4\ (s) + 12H_2$.

Carborization. Carbides of various elements can be used as metallurgical coatings as well as in the formation of optically or electrically active materials. Silicon carbide, SiC, is a material that is used in both applications. SiC is used as a high-temperature electronic material since it is a wide-gap semiconductor. The CVD formation of thin-film SiC proceeds through a variety of means. Hydrocarbons such as propane and methane can be used in conjunction with silane to deposit SiC films, that is, $SiH_4 + CH_4 \Rightarrow SiC + 4H_2$. Organosilane compounds, such as methylsilane, SiH_3CH_3, have also been used as a potential single-source precursor.

Chemical Transport Reaction. The gas-phase reactants that are used in growth may also be produced through a high-temperature chemical reaction. Some of the earliest forms of CVD as applied to the semiconductor industry have been through the chemical transport system. In such a CVD system, a source material, such as Ga metal or Ge, is reacted with hydrogen chloride gas to produce a high-temperature, halide-bearing volatile compound. These reactants formed in an initial or source zone of the reactor are transported to the deposition region by dilution in a carrier gas. The deposition reaction proceeds through the addition of a second reactant to form the compound. Deposition of GaN is carried out by means of chemical transport of Ga with $2Ga(l) + 2HCl(g) \Rightarrow 2GaCl(g) + H_2(g)$. The GaCl(g) thus obtained is then immediately transported to the deposition surface where it deposits GaN in the presence of ammonia: $GaCl(g) + NH_3(g) \Rightarrow GaN(s) + H_2(g) + HCl$. These transport reactions are also used to deposit thin films of a source material. For example, GaAs can react at high temperatures with HCl to again form GaCl(g) and $As_4(g)$ through the reversible reaction:

$$GaAs(s) + HCl(g) \Leftrightarrow GaCl(g) + \tfrac{1}{4}As_4(g) + \tfrac{1}{2}H_2(g)$$

These reaction products are transported to a cooler region of the reactor wherein the wafer is placed. The reverse reaction, driven by the supersaturation of the gas phase due to the lower temperature, results in the deposition of GaAs through the reforming of the source material (8). Thin films of varying electrical conductivity or composition can therefore be deposited by a simple fast means.

Surface Mechanisms

The composition and the flux of species arriving on the surface is determined by the gas-phase reactions and physical conditions of temperature and pressure. The incoming species along with surface structure and possible chemical reactions on the surface determine the type and concentration of the surface species. The processes of adsorption, surface migration, surface reactions, and desorption play major roles in establishing the surface mechanism. The nature of growth surface, such as the surface crystal orientation, imperfections, impurities and structural defects, temperature, and surface chemical composition, all profoundly affect the surface mechanisms and the subsequent film quality. The composition of the substrate and adsorbed contaminants can deleteriously affect the growth rate and also the structural quality of CVD films. Chemical impurities on the substrate surface can act as growth catalysts or inhibitors. In the case of Si deposition from SiH_4, the presence of phosphine, PH_3, can dramatically lower the growth rate under certain growth conditions. The PH_3 adsorbs strongly on the growth front, preventing the reaction of SiH_4 with the surface. Surface contaminants can result in defects such as pinholes, pits, thin spots, blisters, microbubbles, and localized devitrification in the case of amorphous materials.

Often the adsorption of gas-phase species is modeled via simple Langmuir adsorption isotherms, a model based on thermodynamic equilibrium. The rate of adsorption and the steady-state concentration of adsorbed species on the surface depend, in the Langmuir model, on the energy of adsorption, availability and concentration of appropriate adsorption sites, the concentration of all competing gas-phase species, and the surface temperature.

Some gas-phase species appear to dissociatively adsorb, releasing a fragment in the process, whereas other molecules may undergo a simultaneous reaction like β-elimination reaction. Adsorption of $Ga(CH_3)_3$ on GaAs surface during GaAs epitaxy, for example, is accompanied with the release of the $^{\cdot}CH_3$ radical while adsorption of $Ga(C_2H_5)_3$ most likely involves the β-hydride elimination reaction (9). Often rates of adsorption reactions are assumed to be proportional to the rate of collision of gas-phase species with the surface.

There can be direct reactions between gas-phase species and adsorbed species as well as between surface adsorbed species that can lead to deposition. This reaction mechanism is sometimes referred to as an abstraction reaction. The reactive radicals in the gas phase react with the surface radicals, abstracting these adsorbed species and giving off a gas-phase species. In the recombination reactions, two surface species react to regenerate the surface free sites and gives off a gaseous product. Surface species can also be removed by the desorption of surface species. The desorption rate of a surface species depends on its concentration, surface temperature, and bond strength.

The final piece in the mechanism is the surface diffusion of the adsorbed species. This phenomenon, since it is not well understood, is often neglected. It is important in determining the final placement of atoms and hence the structure and crystal quality. The concentration of surface species on the surface is a dynamic balance between the rate of arriving gaseous species interacting with vacant surface sites, the rate of conversion to some other surface species, surface migration, and its desorption rate. The eventual product of these all these reactions, whether in the gas phase or on the surface, is the growth of the film.

Models of CVD Process

> The world can doubtless never be well known by theory: practice is absolutely necessary; but surely it is of great use to a young man, before he sets out for that country, full of mazes, windings, and turnings, to have at least a general map of it, made by some experienced traveler.
>
> *Lord Chesterfield*

The CVD process is very complex: It involves flow, heat, and mass transfer coupled to gas-phase and surface chemical kinetics. Theory of the flow and heat transfer aspects is rather well established. Application of it to the complex reactor systems for practical solutions is not trivial but is doable from the theoretical standpoint, provided that proper computational resources are available and provided that detailed description of the physical system, including conduction in the reactor walls, external and internal radiation in the reactor chamber, external radiation, and convective heat transfer to the ambient, is provided. The present trend is to solve the fluid dynamics problem separately from the chemical reaction and kinetics problem. This is important in nondilute systems. Simplifications, like the boundary layer theory, are being rapidly replaced by the numerical solution of the fundamental fluid flow equations, combined with the energy balances. In spite of the nonequilibrium nature of the process, thermodynamics may be profitably used to determine the feasibility of a particular reaction pathway.

The fluid mechanical model, applicable to most CVD systems operating in the continuum regime, is based on the fundamental equations of mass continuity, momentum balance, and heat or energy balance. The general derivation and form of these equations is found in standard tests on transport phenomena (10). Dynamic effects are considered important only in the context of switching between inlet gas streams during the growth of layered surfaces. The important physical equations are summarized below:

Continuity Equation:

$$\nabla(\rho \nu) = 0$$

where ρ is the gas density and ν is the gas velocity.

Momentum Equation:

$$\rho \nu \cdot \nabla \nu = -\nabla P + \nabla \cdot \mu \left[\nabla \nu + (\nabla \nu)^{\mathrm{T}} - \frac{2}{3} I \nabla \cdot \nu \right] + \rho g$$

where g is the gravitational acceleration, P is the pressure, and μ is the viscosity.

Energy Balance:

$$\rho C_p \nu \cdot \nabla T = \nabla \cdot (k \nabla T)$$

where C_p is the specific heat and k is the thermal diffusivity.

In the above formulation of energy balance, contributions from viscous energy dissipation, Dufour flux, and heats of reaction have been omitted since they are negligible for most CVD conditions. Such heats of reaction may be important in the case when the deposition rates are very high, as in the case of atmospheric-pressure oxide systems. The above equations are coupled to the auxiliary equations of state defining the physical properties in terms of the pressure and temperature. Particularly cold-walled CVD reactors, temperature gradients, and hence gas expansion are significant since they can alter the local gas properties. The local density of the gas, ρ, is connected to the pressure and temperature by ideal gas law. The temperature (and pressure) dependence of viscosity, μ, heat capacity, C_p, and thermal conductivity, k, are the other auxiliary equations needed to complete the mathematical description enabling the calculation of the reactor fluid flow environment.

The Gas-Phase Chemical Reaction and Kinetics Model. Reaction-kinetic model includes the balance over the individual chemical species and is an extension of the overall continuity equation:

$$c\nu \cdot \nabla x_i = \nabla \cdot j_i - \sum_{i=1}^{n} [\nu_{ij} R_j^g]$$

where c is the carrier gas concentration ($c = P/R_gT$), R_g is the ideal gas constant, x_i is the molar fraction of species i, j_i is the diffusion flux, and ν_{ij} is the stoichiometry coefficient of the jth chemical reaction, with R_i^g considered generating or consuming this particular species in the gas phase. The diffusion flux combines Fickian diffusion because of concentration gradients and thermal diffusion, or the Soret effect, resulting from thermal gradients:

$$j_i = cD_{im}(\nabla x_i + k_i^T \nabla \ln T)$$

where k_i^T, a temperature dependent parameter, ∇x_i is the thermal diffusion coefficient for species i, and D_{im} is the multicomponent diffusion coefficient for species i in a mixture m.

Surface Chemistry Model. For each of the surface species, a steady-state balance equation is written following the consumption and generation of the surface species. Additional constraints are provided by the conservation of total number of sites on the surface. The sum of all the surface chemical reactions, leaving a net deposit when coupled to the arrival of species to the growth front, results in the net growth rate of the deposit.

Solving the Model. Solution of the above set of partial differential equations depends on the boundary conditions and is specific to the reactor system being investigated. Normally at solid walls, including the growth surface, no-slip and no-penetration is assumed. The velocity at the inlet is usually specified, and a fully developed flow is assumed at the outlet. These conditions should be carefully implemented lest the solution is rendered meaningless. For example, a fully developed outlet flow may preclude the possibility of return flows at the outlet. The thermal boundary conditions include conduction in the reactor walls, convective (natural and forced) heat transfer to the ambient and radiative heat transfer to the outside world, and radiative coupling between various regions inside the reactor. Thermal boundary conditions have a significant effect on the flow and temperature field. Boundary conditions on the individual gaseous species is straightforward. Net flux to a deposition surface is governed by the surface reactions, and there is no net flux to nonreacting surfaces (Fig. 4).

The above set of nonlinear equations may be solved using one of the many well-established methods used in computational fluid dynamics and combustion problems. Traditionally, finite difference schemes have been popular and have been successfully employed for CVD systems. The finite element method (11) is well suited for complex geometries and application of detailed boundary conditions. Recently, the finite volume approach has also been successfully used.

Many researchers are convinced that the traditional finite element method will not work properly because of its inability to provide "good" results. The "good" results are those that do not have "wiggles" or oscillations and have nothing particu-

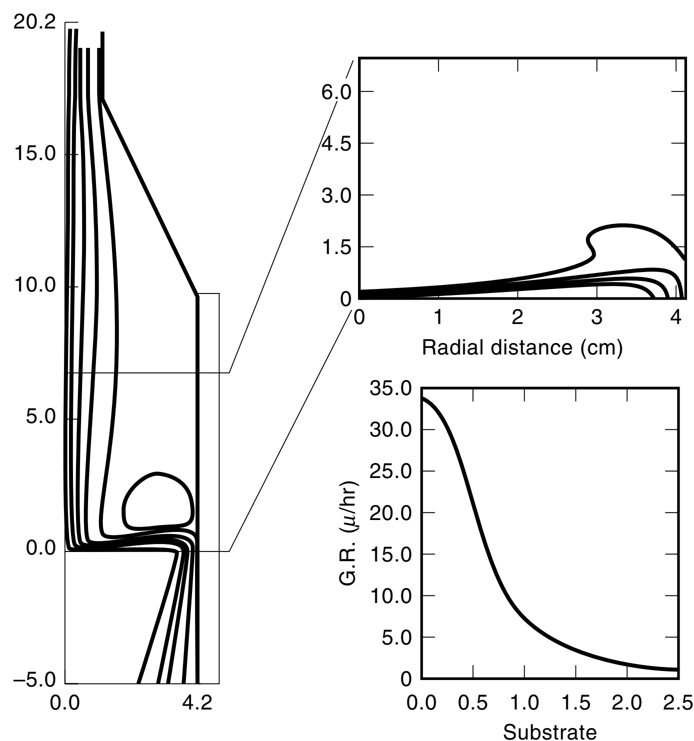


Figure 4. Computational fluid dynamics can be used to predict the detailed flow behavior, thermal profiles, and chemical behavior in the reactor as shown here for the case of growth in a heated vertical, cold-walled reactor. In this case, the thermal profile accompanying this fluid flow reveals a sharp temperature gradient near the substrate surface. The solution of the chemical model results in a prediction of the growth rate over the sample surface. (S. A. Safri, J. M. Redwing, M. A. Tischler, and T. F. Kuech, *J. Electrochem. Soc.,* **144**: 1789–1796, 1997. Reproduced by permission of the Electrochemical Society.)

larly to do with the accuracy of the solution or inappropriateness of the method. Often, these oscillations can be either completely eliminated or at least reduced dramatically, making them insignificant by proper mesh refinement, application of less restrictive boundary conditions at the exit, and extending the computational domain to contain regions of severe gradients well within its boundaries. The advantage of Galerkin finite element method is that it usually "announces" the nature of the difficulty via oscillations if the selected mesh or the boundary condition is inappropriate.

The final model description can be used to predict the thermal, fluid, and chemical profiles within the system. The growth rate can be calculated, and these models can be used to predict the performance of the reactor without the costly expense of the experimental optimization of the reactor.

SUMMARY

Chemical vapor deposition (CVD) is a versatile thin-film deposition technique. The use of CVD has extended to the deposition all of the critical materials used in the manufacture of electronic devices. Through the choice of the chemical system and reactor design metals, dielectrics and semiconductors can be deposited in a variety of physical forms, namely, crystalline and amorphous materials. The ability to design reactors and control the chemical, fluid, and thermal environment during the film deposition through the development of process models has allowed controlled growth of thin films. CVD can be used to uniformly deposit thin films of semiconductor layers as thin as 1 nm through rapid changes in the gas-phase composition. As the size of the semiconductor wafers increases, the development of the CVD reactor will center on the use of large single-wafer systems that will present a new challenge to the engineering of these large deposition systems.

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CHEMISTRY, PLASMA. See PLASMA CHEMISTRY.
CHILLED WATER STORAGE. See THERMAL ENERGY STORAGE.
CHIP-SCALE SEMICONDUCTOR PACKAGING RELIABILITY. See PACKAGING RELIABILITY, CHIP-SCALE SEMICONDUCTOR.
CHIPS, NEURAL. See NEURAL CHIPS.