CHEMICAL VAPOR DEPOSITION

1. Introduction

Vapor deposition is a process that transfers gaseous molecules into solid-state materials (Fig. 1). From this process, thin films can be grown on substrates and fine powders can be formed. There are two major types of vapor depositions, physical vapor deposition (PVD, see THIN FILMS, FILM FORMATION TECHNIQUES) (1) and chemical vapor deposition (CVD) (2–4). The difference is that in a PVD process, a source is vaporized to deposit the film. Usually, the deposited film is the same as the source material. This vaporization–deposition process is a physical process that involves phase change but does not typically involve a chemical reaction. Major PVD techniques are vacuum evaporation, sputtering, ion plating, and molecular beam epitaxy (MBE) (see THIN FILMS, FILM FORMATION TECHNIQUES). In the CVD process (Fig. 2), a molecular source, frequently called a precursor, is vaporized into a flow reactor. The precursor is activated by a form of energy and decomposed through steps of chemical reactions to deposit thin films. The

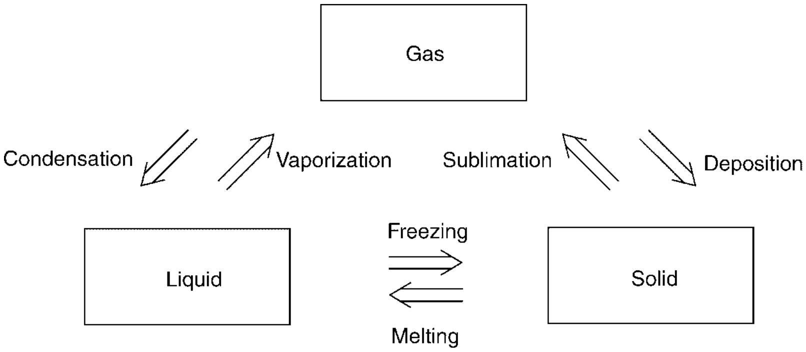

Fig. 1. Definition of deposition.

CVD processes are complex because there are many variables, such as temperature, pressure, chemical nature of the precursor, physical shape of the reactor, etc, to be controlled. Consequencetly, the physical and chemical properties of the films grown may vary widely from one reactor system to another. Using CVD technology, it is possible to grow thin films of metals (5), semiconductors (6), and insulators (7). This process is used extensively to produce semiconductor devices (see INTEGRATED CIRCUITS; LIGHT-EMITTING DIODES; LIGHT GENERATION SEMICONDUCTOR LASERS) (8), and protective coatings on precision machine parts (see METALLIC COATINGS, SURVEY) such as diamond films (9). Recently, CVD has been used to grow nanotubes, nanorods, and nanowires (see NANOTECHNOLOGY) of many materials (10–12).

In a typical CVD system, there are three major components to be considered: the precursors, the substrate, and the reactor. The precursors are the volatile molecules that will deposit thin film materials inside the reactor. The substrate provides a foundation for the film to grow upon. The reactor, usually a flow reactor (see REACTOR TECHNOLOGY), allows the deposition reaction to proceed. The precursors are supplied into the reaction zone of the reactor through a delivery system. Upon arrival, the precursors are activated and decomposed to deposit thin films on the substrates placed inside the reactor. Vapor-phase byproducts are removed and treated if necessary (see EXHAUST CONTROL, INDUSTRIAL). More descriptions are provided below.

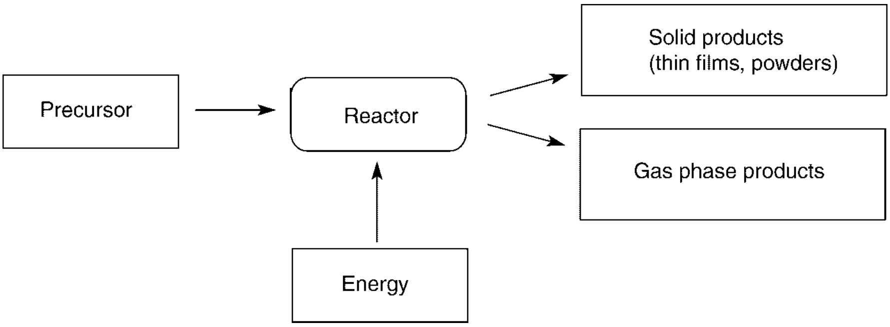

Fig. 2. Schematic diagram of CVD Process.

Table 1. **Some Common Precursors and Corresponding Thin Films Grown by CVD**

Precursor[a]	Thin films by CVD
hydrides, MH_x (see HYDRIDES)	
SiH_4	Si and Si containing materials (see SILICON COMPOUNDS, SILANES; SILICON, PURE)
$AlH_3(NMe_3)_2$	Al and Al containing materials (see ALUMINUM AND ALUMINUM ALLOYS)
NH_3	nitrides (see AMMONIA; NITRIDES)
PH_3	phosphides (see PHOSPHINE AND ITS DERIVATIVES)
halides, MX_y	
$SiCl_4$	Si and Si containing materials (see SILICON COMPOUNDS, SILICON HALIDES; SILICON, PURE)
$GeCl_4$	Ge and Ge containing materials (see GERMANIUM AND GERMANIUM COMPOUNDS)
$TiCl_4$	Ti and Ti containing materials (see TITANIUM AND TITANIUM ALLOYS)
$TaCl_5$	Ta and Ta containing materials (see TANTALUM AND TANTALUM COMPOUNDS)
MoF_6	Mo and Mo containing materials (see MOLYBDENUM AND MOLYBDENUM ALLOYS; MOLYBDENUM COMPOUNDS)
WF_6	W and W containing materials (see TUNGSTEN AND TUNGSTEN ALLOYS; TUNGSTEN COMPOUNDS)
metal-organics metal alkyls	
$AlMe_3$	Al and Al containing materials (see ALUMINUM AND ALUMINUM ALLOYS)
$Al\textit{i}\text{-}Bu_3$	Al and Al containing materials (see ALUMINUM AND ALUMINUM ALLOYS)
$Ti(CH_2\textit{t}\text{-}Bu)_4$	Titanium carbide and other Ti containing materials (see TITANIUM AND TITANIUM ALLOYS)
metal alkoxides (see ALKOXIDES, METAL)	
$Ti(O\textit{i}\text{-}Pr)_4$	TiO_2 (see TITANIUM COMPOUNDS, INORGANIC)
$[Cu(O\textit{t}\text{-}Bu)]_4$	Cu and Copper Oxides (see COPPER; COPPER COMPOUNDS)
metal dialkylamides	
$Ti(NMe_2)_4$	titanium nitride and carbonitride (see TITANIUM COMPOUNDS, INORGANIC; NITRIDES; CARBIDES, INDUSTRIAL HARD)
$Cr(NEt_2)_4$	chromium nitride and carbonitride (see CHROMIUM AND CHROMIUM ALLOYS; NITRIDES; CARBIDES, INDUSTRIAL HARD)
metal diketonates	
$Cu(acac)_2$	Cu and Copper Oxides (see COPPER; COPPER COMPOUNDS)
$Pt(hfac)_2$	Pt (see PLATINUM-GROUP METALS; PLATINUM-GROUP METALS, compounds)
metal carbonyls (see METAL CARBONYLS)	
$Fe(CO)_5$	Fe (see METAL CARBONYLS; IRON COMPOUNDS; IRON)
$Ni(CO)_4$	Ni (see METAL CARBONYLS; NICKEL AND NICKEL ALLOYS; NICKEL COMPOUNDS)

[a] acac = Acetylacetonato and hfac = hexafluoroacetylacetonato.

2. Precursors and Delivery System

Traditionally, volatility is the most important factor for selecting a CVD precursor. However, suitable simple molecules with high vapor pressure are relatively rare. Thus, only limited types of materials can be deposited by CVD.

Recently, the search for new CVD precursors has been an active research area. Many new precursors have been synthesized. Generally, the volatility of a molecule is determined by its molecular weight and molecularity (degree of polymerization). The volatility, the result of basic molecular structure and bonding, is a property difficult to predict and adjust. Other characteristics to be considered for choosing a suitable CVD precursor are the stability and reactivity, usually defined by the bond strength. An ideal precursor needs to be stable in storage and in delivery into the reactor. Also, it needs to be reactive enough to deposit thin films at low temperatures so that more substrates can be chosen. However, these two characteristics are in conflict. For example, high stability frequently means low reactivity; consequently, a high temperature of deposition is required. This limits the selection of the substrate materials to be deposited on. Thus, a compromise between the stability and the reactivity is frequently needed. Safety is another important issue. Many CVD precursors are toxic, poisonous, or flammable in the air. Their volatility suggests that fast diffusion of the precursor molecules in the space is likely. Thus, great caution should be paid to handling of CVD precursors. Some common precursors and the deposited materials are given in Table 1. Frequently, more than one precursor is needed to grow materials containing mixed elements. In addition to the precursors listed in Table 1, there are many other precursors with mixed ligands.

The precursor delivery system usually has flow controllers (see FLOW MEASUREMENT) to monitor and to adjust the quantities of the gaseous reactants and the carrier gases supplied. For liquid precursors, temperature-controlled bubblers are used. Solid precursors can be delivered using temperature-controlled evaporators. Solid precursors with extremely low vapor pressures can be dissolved in solutions and supplied to the reactor through a solution delivery system.

3. CVD Reactors

CVD reactors are constructed from temperature and chemical resistant materials such as quartz and stainless steel. A source of energy is provided and controlled to supply thermal (see TEMPERATURE MEASUREMENT), plasma (see PLASMA TECHNOLOGY) or photo (see PHOTOCHEMICAL TECHNOLOGY SURVEY) energy to the reactor. The thermal energy can be supplied from resistively heated elements (see FURNACES, ELECTRIC, RESISTANCE FURNACES) inside or outside the reactor, called cold-wall and hot-wall reactors, respectively. The reactors can be heated inductively (see FURNACES, ELECTRIC, INDUCTION FURNACES) also. In addition, a focused laser beam can be used to heat a small area. This method is called laser CVD (LCVD) (13). Depending on the thermal stability of the precursor and the substrate, the temperature of deposition of thermal CVD can be anywhere between

350 and 2000 K. Room temperature deposition is possible with some processes, particularly with plasmas.

The pressure of deposition can vary widely. When the CVD process is carried out under atmospheric pressure, it is frequently called "atmospheric pressure CVD" (APCVD). In many cases, a vacuum system (see VACUUM TECHNOLOGY; PUMPS) is attached to the reactor to maintain a suitable deposition pressure (see PRESSURE MEASUREMENT) usually <100 Torr (1.33×10^4 Pa). This technique is classified as "low pressure CVD" (LPCVD). Chemical beam epitaxy (CBE) is a technique similar to MBE. It uses molecular chemicals precursors instead of elemental solids to generate molecular beams (or chemical beams) to deposit thin films under extremely low pressures ($< 10^{-9}$ Torr or 1.33×10^{-7} Pa).

Plasma (glow discharge) is another form of energy frequently used in CVD. The technique is called plasma-enhanced CVD (PECVD) or plasma-assisted CVD (PACVD) (14). Inside the discharge zone, partially ionized gas composed of ions, electrons, and neutral species are generated. Chemical interactions among these active species and the substrate frequently deposit non-stoichiometric thin films with unique properties at low temperatures. PECVD is a more complex technology than the thermal CVD mentioned above. Usually, PECVD is carried out at low pressures to generate low temperature plasma. In addition to the factors, such as pressure and temperature, mentioned for the thermal CVD, many other parameters have to be considered. These include, eg, the frequency and the power supplied to induce the glow discharge process, and the shape and position of the electrodes and coils. Photon energy from light sources, such as discharge tubes and lasers, is another form of energy that can be used for low temperature CVD processes. The technique is called photo CVD (PCVD) (15). Several types of reactors are given as examples.

3.1. Horizontal Hot-Wall Reactor. The simplest type of CVD reactor is shown in Figure 3. It can be constructed easily from a tube furnace and a quartz tube. It is called "hot-wall" because the furnace outside heats the tube wall. The flow pattern is horizontal and parallels the way the substrates are arranged.

3.2. Vertical Cold-Wall Reactor. As shown in Fig. 4, the substrates are heated by the heating stage inside the reactor. The reactor is called "cold-wall" because the reactor wall has a temperature lower than the central heating stage. The flow pattern is vertical and perpendicular to the substrates.

3.3. Parallel Plate Plasma Reactor. In addition to the basic features of the cold-wall reactor discussed above, this reactor (Fig. 5) has a radio frequency

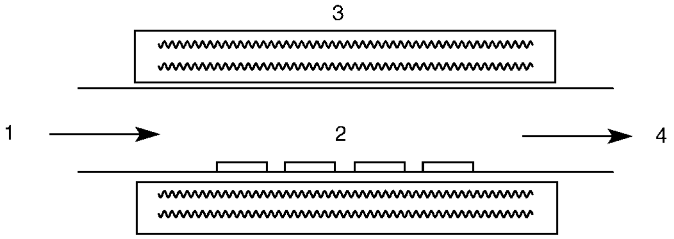

Fig. 3. Horizontal hot-wall reactor. 1: precursor in; 2: substrates; 3: heater or furnace; 4: exhaust.

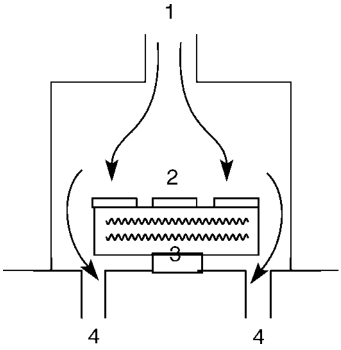

Fig. 4. Vertical cold-wall reactor. 1: precursor in; 2: substrates; 3: heater; 4: exhaust.

(rf) power supply. (Other frequency ranges are also possible.) It provides an electric field through a pair of parallel electrodes to generate glow discharge under low pressure. The substrates, placed between the electrodes, are in the glow discharge zone. Because the substrates are placed in the plasma zone, possible radiation damage from the active species in the plasma to the deposited films is a drawback.

3.4. Inductive Tube Remote Plasma Reactor.

This reactor (see Fig. 6) has similar features the parallel plate plasma reactor; however, the plasma is generated by an induction coil outside the reactor. The substrates are placed away from the discharge zone, which is why it is called "remote plasma reactor". In this way, radiation damage can be significantly reduced.

In many CVD processes, the precursors and the vapor-phase by-products are frequently hazardous chemicals. They can be poisonous, flammable, and corrosive. Thus, proper treatment is necessary before they can be discharged to the environment. The most common methods are to decompose, adsorb, or remove them using catalytic crackers, traps and scrubbers (see EXHAUST CONTROL, INDUSTRIAL).

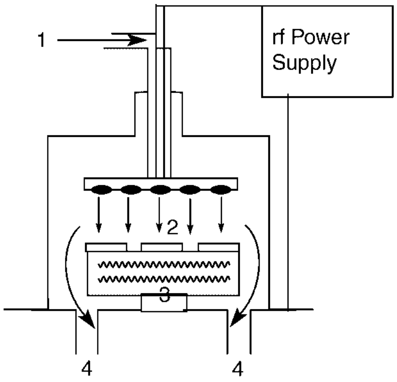

Fig. 5. Parallel plate plasma reactor. 1: precursor in; 2: substrates; 3: heater; 4: exhaust.

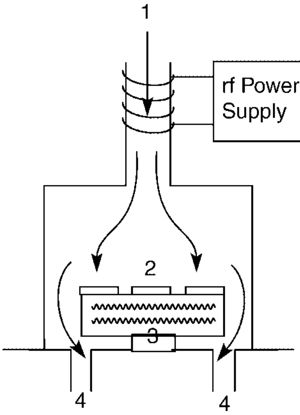

Fig. 6. Inductive tube remote plasma reactor. 1: precursor in; 2: substrates; 3: heater; 4: exhaust.

4. Substrates

One advantage of CVD is that thin films can grow on complicated shapes, which is due to the fact that if the molecular diffusion rate is faster than the kinetic decomposition rate the precursor molecules can diffuse from the flow stream to the surface of the substrates uniformly. Since the thin film grows directly on the surface of the substrates, the surface preparation is very important. The substrate can be cleaned either by physical methods or chemical methods. Physical methods include high pressure scrubbing and liquid spraying, ultrasonic cleaning, centrifugal cleaning, solvent treatment, extraction and vapor degreasing, thermal desorption, sublimation, and sputtering. Examples of chemical methods are oxidation (thermal and wet) and stripping, chelating and complexion, solution (wet) and vapor etching, plasma etching, and ultraviolet (uv) irradiation. It is better to clean the substrates right before deposition. If they are not used immediately, they should be stored in a clean environment to avoid recontamination. The selection of substrate materials in a thermal CVD process is limited by their high temperature stability and compatibility with the deposited film. On the other hand, PECVD can deposit thin films at much lower temperatures, which offers more substrate selections. However, at much lower temperatures often the quality of the films is poorer; eg, adherence and crystallinity.

5. Fundamental Principles

5.1. Thermodynamics.

Like most chemical reactions, it is possible to establish theoretical feasibility for a CVD reaction by calculating the Gibbs energy of reaction and the equilibrium constant (see THERMODYNAMICS). In general, an ideal gas mixture in contact with pure condensed phases is assumed for the calculations. However, the prediction is of somewhat limited use, as the vast majority of CVD reactions are inherently nonequilibrium because they are

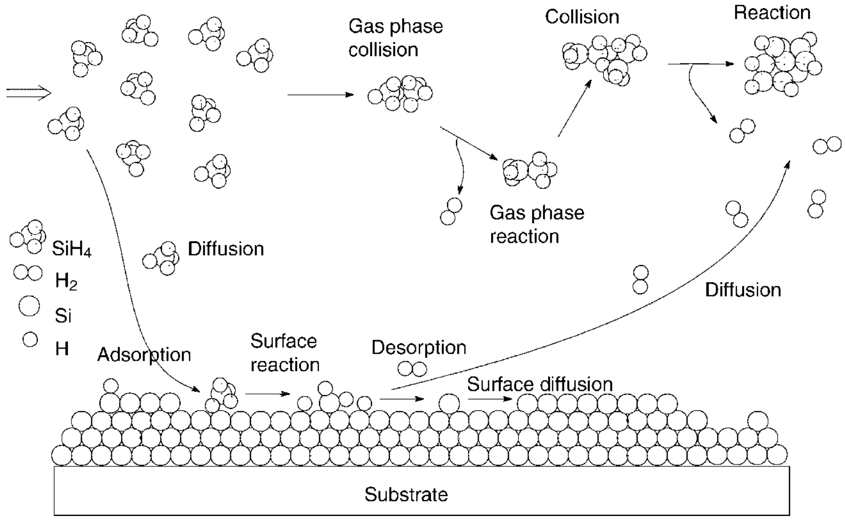

Fig. 7. Reaction steps of Si thin-film and particle growth from SiH_4.

carried out in flow reactors under conditions where there are significant growth rates and volatile by-products are removed constantly. However, CVD kinetics (see KINETIC MEASUREMENTS) is far more important than the thermodynamics.

5.2. Kinetics. Growth of the thin film in a CVD process, after the precursor molecules are delivered into the reactor, is the result of several basic steps. These steps are presented in Figure 7, using CVD of Si from SiH_4 as an example.

- Diffusion of precursor to the surface.
- Gas-phase reactions of the precursor.
- Adsorption–desorption of precursor at the surface.
- Reaction of adsorbed precursor on the surface.
- Incorporation of surface atoms into the bulk via surface diffusion.
- Desorption–adsorption and diffusion of the surface reaction by-products.

If the precursor concentration is high so that the diffusion rate is low, or if the reaction temperature is high, powders could form through a gas phase nucleation process. Collisions of the precursor molecules and gas-phase reactions might then take place resulting in the enlargement of particles' size.

In a CVD system, the overall reaction rate is influenced by the rates of precursor's feed, diffusion, surface as well as gas-phase reactions. The rate limiting cases are discussed below.

Feed-Rate-Limited CVD. In this case, the film growth rate is limited by the amount of the precursor molecules delivered into the reactor. This is frequently encountered for precursors with low vapor pressure and fast reaction on the surfaces. In the extreme case, the quantity of the reacted precursor equals the quantity of the precursor introduced. The film growth rate appears to be almost independent of deposition temperature, which is true for diffusion controlled

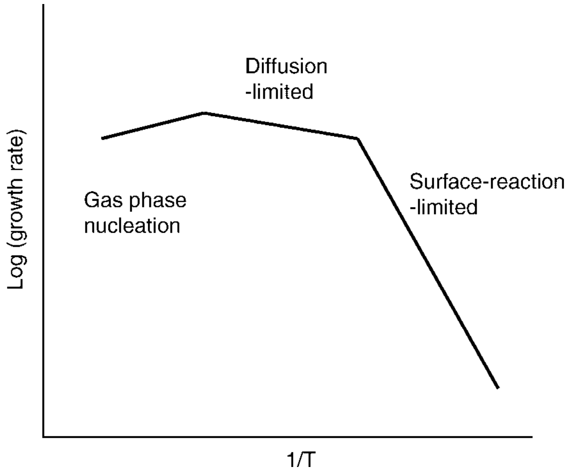

Fig. 8. Arrhenius plot of thin-film growth by CVD.

processes too, because the surface reaction rate is much higher than the feed rate.

Diffusion and Surface-Reaction-Limited CVD. These are dominant when the precursor feed rate is sufficiently high. Diffusion limited CVD, or as it frequently called diffusion-controlled or mass-transfer-controlled, is rate limiting when the surface reaction rate is high enough so that the growth rate of the film is limited by the diffusion rate of the reactants to the surface. This usually proceeds at high pressure, typically atmospheric pressure, and higher temperatures. On the other hand, the growth rate of the film is limited by the surface reaction rate when the precursor diffusion (transport) to the surface is relatively high. It is then referred to as surface reaction limited CVD, surface-reaction-controlled or kinetic-controlled. This usually occurs at low pressure, typically <10 Torr (1.33×10^3 Pa), and lower temperatures. An Arrhenius plot (see KINETIC MEASUREMENTS) is sometimes useful to differentiate the two cases (Fig. 8). The apparent energy of activation (E_a) can be derived from the slop of the plot to distinguish them. The surface-reaction-limited cases show steeper slope and larger E_a than the diffusion-limited cases. At high temperature (small $1/T$), it is common to observe decreased growth rate due to the increased rate of nucleation in the gas phase, which depletes the reactant concentration and lowers the thin-film growth rate.

In general, mass-transfer rate of the reactant gases to the substrate surface is more influential for APCVD than other CVD techniques. Mass transfer of gases involves the diffusion of molecules across the slow-moving boundary layer above substrate surface. The mass-transfer rate depends on the reactant concentration, the boundary layer thickness, and the diffusivity of the gases. In APCVD, mass-transfer rate and surface reaction rate are of the same order of magnitude. The substrates must lay side by side in the reactor to attain uniform film thickness.

In LPCVD, the mass-transfer rate of the reactant gases to the substrate surface is greatly enhanced due to the increased mean-free path. (Diffusivity is proportional to $1/P$) Here, the surface reaction rate, which is dependent on the reactant concentration and the temperature, controls the rate of deposition. In contrast to APCVD, the substrates can be arranged close-spaced and vertically in LPCVD and still be coated uniformly.

Surface Reactions. The basic CVD reaction steps on a surface can be described by surface adsorption (see ADSORPTION, FUNDAMENTALS), reaction and desorption, as shown in Figure 7. The model is closely related to the Langmuir-Hinshelwood Mechanism frequently used to describe heterogeneous catalysis on the surfaces (see CATALYSIS) (16–18). The composition of the thin films and the fundamental surface reaction steps are studied using surface science analysis techniques (see SURFACE AND INTERFACE ANALYSIS) (18).

6. Conclusions

Just like PVD, CVD is an important and versatile technique to grow high quality thin solid films for many applications. In general, PVD is the preferred method of deposition in many industrial settings. The reason is that CVD is a more complicated process than PVD because the equipment setup is more complex and the chemical reaction steps are more difficult to control. However, the capability of conformal deposition of thin films on complex structures by CVD is the most important advantage of CVD over PVD. Thus, CVD and PVD methods complement each other.

CVD is a bottom-up method of fabrication. It converts small molecules, or building blocks, into extended structures such as thin films. Recently, it has been found that in addition, many nano-sized materials in other shapes, such as particles, tubes, wires, and rods, can be grown effectively by CVD. Thus, CVD is expected to play an important role in the development of the ever-important area of nanotechnology (see NANOTECHNOLOGY).

BIBLIOGRAPHY

1. J. E. Mahan, *Physical Vapor Deposition of Thin Films*, Wiley-Interscience, New York, 2000.
2. M. L. Hitchman and K. F. Jensen, eds., *Chemical Vapor Deposition: Principles and Applications*, Academic Press, London, 1993.
3. H. O. Pierson, *Handbook of Chemical Vapor Deposition: Principles, Technology and Applications*, 2nd ed., Noyes Publications, Norwich, New York, 1999.
4. C. E. Morosanu, *Thin Films by Chemical Vapour Deposition*, Elsevier, Amsterdam, The Netherlands, 1990.
5. T. T. Kodas and M. J. Hampden-Smith, *The Chemistry of Metal CVD*, VCH, Weinheim, 1994.
6. A. C. Jones and P. O'Brien, *CVD of Compound Semiconductors: Precursor Synthesis, Development and Applications*, VCH, Weinheim, 1997.
7. W. S. Rees, ed., *CVD of Nonmetals*, VCH, Weinheim, 1996.
8. A. Sherman, *Chemical Vapor Deposition for Microelectronics: Principles, Technology, and Applications*, Noyes Publications, Park Ridge, New Jersey, 1987.
9. K. E. Spear and J. P. Dismukes, eds., *Synthetic Diamond: Emerging CVD Science and Technology*, Wiley-Interscience, New York, 1994.

10. W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).
11. X. T. Zhou, N. Wang, H. L. Lai, H. Y. Peng, I. Bello, N. B. Wong, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.* **74**, 3942 (1999).
12. T. I. Kamins, R. Stanley Williams, D. P. Basile, T. Hesjedal, and J. S. Harris, *J. Appl. Phys.* **89**, 1008 (2001).
13. J. Mazumder and A. Kar, *Theory and Application of Laser Chemical Vapor Deposition*, Plenum Press, New York, 1995.
14. S. Sivaram, *Chemical Vapor Deposition: Thermal and Plasma Deposition of Electronic Materials*, Van Nostrand Reinhold, New York, 1995.
15. J. G. Eden, *Photochemical Vapor Deposition*, Wiley-Interscience, New York, 1992.
16. R. P. H. Gasser, *An Introduction to Chemisorption and Catalysis by Metals*, Oxford University Press, New York, 1985.
17. G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces*, Cornell University Press, Ithaca, 1981.
18. G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley-Interscience, New York, 1994.

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