

HANDBOOK OF CHEMICAL VAPOR DEPOSITION (CVD)

Principles, Technology, and Applications
Second Edition

by

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Fundamentals of Chemical Vapor Deposition

1.0 INTRODUCTION

Chemical vapor deposition is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit. The CVD technology combines several scientific and engineering disciplines including thermodynamics, plasma physics, kinetics, fluid dynamics, and of course chemistry. In this chapter, the fundamental aspects of these disciplines and their relationship will be examined as they relate to CVD.

The number of chemical reactions used in CVD is considerable and include thermal decomposition (pyrolysis), reduction, hydrolysis, disproportionation, oxidation, carburization, and nitridation. They can be used either singly or in combination (see Ch. 3 and 4). These reactions can be activated by several methods which are reviewed in Ch. 5. The most important are as follows:

- Thermal activation which typically takes place at high temperatures, i.e., $>900^{\circ}\text{C}$, although the temperature can also be lowered considerably if metallo-organic precursors are used (MOCVD).

- Plasma activation which typically takes place at much lower temperatures, i.e., 300–500°C.
- Photon activation, usually with shortwave ultraviolet radiation, which can occur by the direct activation of a reactant or by the activation of an intermediate .

Until recently, most CVD operations were relatively simple and could be readily optimized experimentally by changing the reaction chemistry, the activation method, or the deposition variables until a satisfactory deposit was achieved. It is still possible to do just that and in some cases it is the most efficient way to proceed. However, many of the CVD processes are becoming increasingly complicated with much more exacting requirements, which would make the empirical approach too cumbersome.

1.1 Theoretical Analysis

A theoretical analysis is, in most cases, an essential step which, if properly carried out, should predict any of the following:

- Chemistry of the reaction (intermediate steps, by-products).
- Reaction mechanism.
- Composition of the deposit (i.e., stoichiometry).
- Structure of the deposit (i.e., the geometric arrangement of its atoms).

This analysis may then provide a guideline for an experimental program and considerably reduce its scope and save a great deal of time and effort.

Such an analysis requires a clear understanding of the CVD process and a review of several fundamental considerations in the disciplines of thermodynamics, kinetics, and chemistry is in order. It is not the intent here to dwell in detail on these considerations but rather provide an overview which should be generally adequate. More detailed investigations of the theoretical aspects of CVD are given in Refs. 1–3.

2.0 THERMODYNAMICS OF CVD

A CVD reaction is governed by *thermodynamics*, that is the driving force which indicates the direction the reaction is going to proceed (if at all), and by *kinetics*, which defines the transport process and determines the rate-control mechanism, in other words, how fast it is going.

Chemical thermodynamics is concerned with the interrelation of various forms of energy and the transfer of energy from one chemical system to another in accordance with the first and second laws of thermodynamics. In the case of CVD, this transfer occurs when the gaseous compounds, introduced in the deposition chamber, react to form the solid deposit and by-products gases.

2.1 ΔG Calculations and Reaction Feasibility

The first step of a theoretical analysis is to ensure that the desired CVD reaction will take place. This will happen if the thermodynamics is favorable, that is if the transfer of energy—the free-energy change of the reaction known as ΔG_r —is negative. To calculate ΔG_r , it is necessary to know the thermodynamic properties of each component, specifically their free energies of formation (also known as Gibbs free energy), ΔG_f . The relationship is expressed by the following equation:

$$\text{Eq. (1)} \quad \Delta G_r^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

The free energy of formation is not a fixed value but varies as a function of several parameters which include the type of reactants, the molar ratio of these reactants, the process temperature, and the process pressure. This relationship is represented by the following equation:

$$\text{Eq. (2)} \quad \Delta G_r = \Delta G_f^\circ + RT \ln Q$$

where: $\Delta G_r^\circ = \sum z_i^i \Delta G_{f,i}^\circ$
 z_i = stoichiometric coefficient of species “i” in the CVD reaction (negative for reactants, positive for products)

$\Delta G_{f,i}^\circ$ = standard free energy of formation of species “i” at temperature T and 1 atm.

R = gas constant

T = absolute temperature

$$Q = \prod_i a_i^{z_i}$$

a_i = activity of species “i” which is = 1 for pure solids and = $p_i = x_i P_T$ for gases

p_i = partial pressure of species “i”

x_i = mole fraction of species “i”

P_T = total pressure

By definition, the free energy change for a reaction at equilibrium is zero, hence:

$$\text{Eq. (3)} \quad \Delta G = - RT \ln K$$

(K is the equilibrium constant)

It is the equilibrium conditions of composition and activities (partial pressure for gases) that are calculated to assess the yield of a desired reaction.

A demonstration of the feasibility of a reaction is illustrated in the following example regarding the formation of titanium diboride using either diborane or boron trichloride as a boron source, as shown in the following reactions:



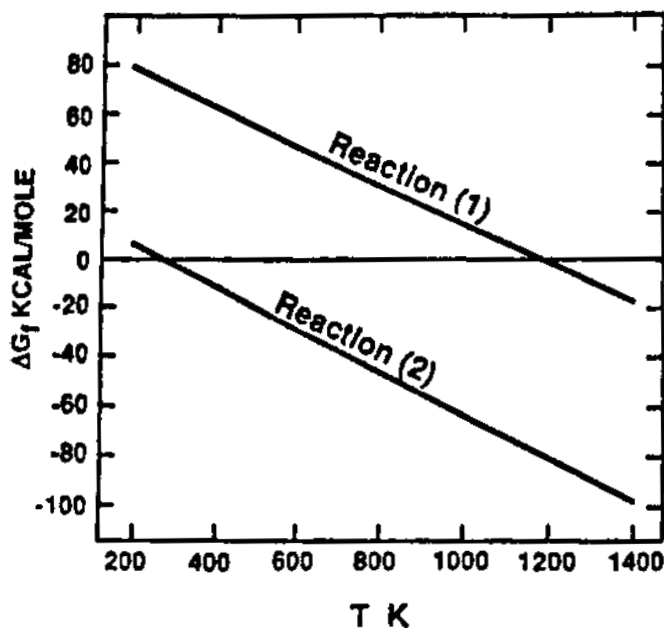


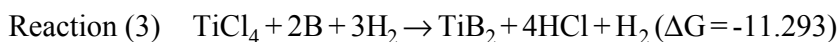
Figure 2.1. Changes in free energy of formation for TiB_2 deposition in the following reactions: (1) $\text{TiCl}_4 + 2\text{BCl}_3 \rightarrow \text{TiB}_2 + 10\text{HCl}$; (2) $\text{TiCl}_4 + \text{B}_2\text{H}_6 \rightarrow \text{TiB}_2 + \text{H}_2$.

The changes in free energy of formation of Reaction (1) are shown in Fig. 2.1 as a function of temperature.^[4] The values of ΔG_r were calculated using Eq. (1) above for each temperature. The Gibbs free-energy values of the reactants and products were obtained from the JANAF Tables.^[5] Other sources of thermodynamic data are listed in Ref. 6. These sources are generally accurate and satisfactory for the thermodynamic calculations of most CVD reactions; they are often revised and expanded.

TiB_2 can also be obtained using diborane as a boron source as follows:



The changes in the free energy of formation on this reaction are shown in Fig. 2.1. It should be noted that the negative free energy change is a valid criterion for the feasibility of a reaction only if the reaction, as written, contains the major species that exist at equilibrium. In the case of Reaction (2), it is possible that B_2H_6 has already decomposed to boron and hydrogen and the equilibrium of the reaction might be closer to:



As can be seen in Fig. 2.1, if the temperature is raised sufficiently, ΔG_r becomes negative and the diborane reaction proceeds at a much lower temperature than the boron trichloride reaction.

2.2 Thermodynamic Equilibrium and Computer Programs

Reactions (1) and (2) above are actually greatly simplified. In reality, it is likely that subchlorides such as $TiCl_3$ and $TiCl_2$ will be formed in Reaction (1) and higher boranes in Reaction (2). Such factors are not revealed by the simple free-energy change calculations.

In many cases, a more complete understanding of CVD reactions and a better prediction of the results are needed and a more thorough thermodynamic and kinetic investigation is necessary. This is accomplished by the calculation of the thermodynamic equilibrium of a CVD system, which will provide useful information on the characteristics and behavior of the reaction, including the optimum range of deposition conditions.

The calculation is based on the rule of thermodynamics, which states that a system will be in equilibrium when the Gibbs free energy is at a minimum.^[7] The objective then is the minimization of the total free energy of the system and the calculation of equilibria at constant temperature and volume or at constant pressure.^[8] It is a complicated and lengthy calculation but, fortunately, several computer programs are now available that considerably simplify the task.^[9]

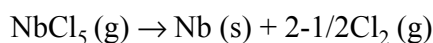
Such programs include SOLGASMIX, which was developed by Erikson and Besmann^{[10][11]} and EKVICALC and EKVIBASE, developed by Nolang.^[12] These programs are now used widely in equilibrium calculations in CVD systems. To operate them, it is first necessary to identify all the possible chemical species, whether gaseous or condensed phases, that might be found in a given reaction. The relevant thermodynamic properties of these phases are then entered in the program as input data. If properly performed, these calculations will provide the following information:

- The composition and amount of deposited material that is theoretically possible under any given set of deposition conditions, that is at a given temperature, a given pressure and given input concentration of reactants.
- The existence of gaseous species and their equilibrium partial pressures.
- The possibility of multiple reactions and the number and composition of possible solid phases, with the inclusion of the substrate as a possible reactant.
- The likelihood of a reaction between the substrate and the gaseous or solid species.

All of this is valuable information, which can be of great help. Yet, it must be treated with caution since, in spite of all the progress in thermodynamic analysis, the complexity of many CVD reactions, is such that predictions based on thermodynamic calculations, are still subject to uncertainty. As stated above, these calculations are based on chemical equilibrium which is rarely attained in CVD reactions.

It follows that, in order to provide a reliable and balanced investigation, it is preferable to combine the theoretical calculations with an experimental program and, hopefully, they will correlate. Fortunately, laboratory CVD experiments are relatively easy to design and carry out; they do not require expensive equipment and results can usually be obtained quickly and reliably.

A classic example, combining theoretical study and laboratory experiments, is the deposition of niobium, originally described by Blocher.^[13] The following reaction was used:



In Fig. 2.2, the critical deposition temperature of NbCl_5 , as a function of its initial pressure, is shown from experimental data from Blocher and the author. There are two temperature-pressure regions, which are separated by a straight line. The metal is deposited only in the region below the line. Above, there is no deposition. The line is a least-square fit of the data. Its position was confirmed using the SOLGASMIX computer program.

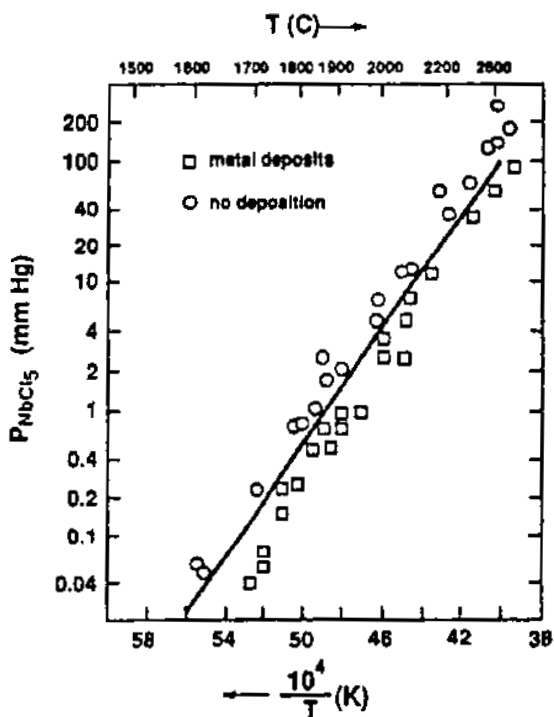


Figure 2.2. Critical deposition temperature of niobium as a function of NbCl_5 initial pressure.

This example shows the great degree of flexibility that can be obtained in CVD if a proper understanding of the thermodynamics and kinetics is gained. In this particular case, it was possible to deposit a uniform layer of NbC on a graphite rod simply by limiting the reaction to the deposition of the metal. Since the carbide could only be formed using the substrate as a carbon source, the rate was controlled by the diffusion rate of the carbon through the coating and deposition uniformity was achieved over the length of the graphite rod.

3.0 KINETICS AND MASS-TRANSPORT MECHANISMS

3.1 Deposition Sequence

As shown above, a thermodynamic analysis indicates what to expect from the reactants as they reach the deposition surface at a given temperature. The question now is, how do these reactants reach that deposition surface? In other words, what is the mass-transport mechanism? The answer to this question is important since the phenomena involved determines the reaction rate and the design and optimization of the CVD reactor.

It should be first realized that any CVD process is subject to complicated fluid dynamics. The fluid, in this case a combination of gases, is forced through pipes, valves, and various chambers and, at the same time, is the object of large variations in temperature and to a lesser degree of pressure before it comes in contact with the substrate where the deposition reaction takes place. The reaction is heterogeneous which means that it involves a change of state, in this case from gaseous to solid.

In some cases, the reaction may take place before the substrate is reached while still in the gas phase (gas-phase precipitation) as will be reviewed later. As can be expected, the mathematical modeling of these phenomena can be complicated.

The sequence of events taking place during a CVD reaction is shown graphically in Fig. 2.3 and can be summarized as follows:^[1]

- Reactant gases enter the reactor by forced flow.
- Gases diffuse through the boundary layer.
- Gases come in contact with surface of substrate.
- Deposition reaction takes place on surface of substrate.
- Gaseous by-products of the reaction are diffused away from the surface, through the boundary layer.

These steps occur in the sequence shown and the slowest step determines the deposition rate. The rules of the boundary layer apply in most CVD depositions in the viscous flow range where pressure is relatively high. In cases where very low pressure is used (i.e., in the mTorr range), the rules are no longer applicable.

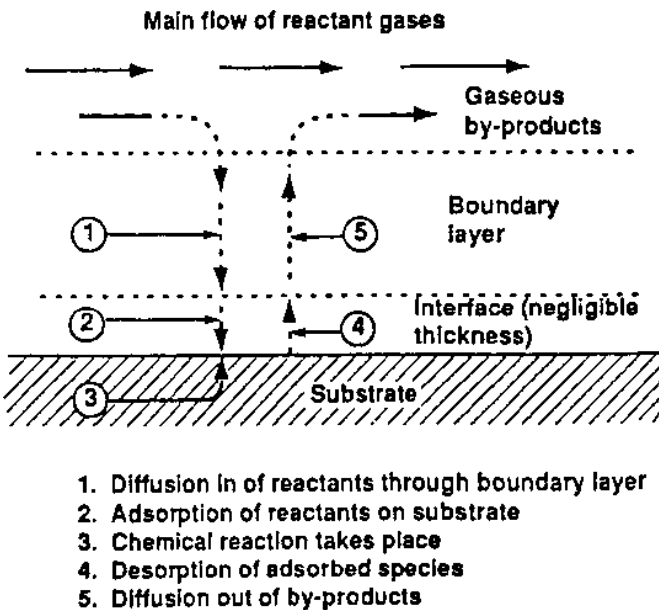
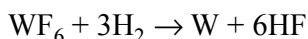


Figure 2.3. Sequence of events during deposition.

3.2 Deposition in a CVD Flow Reactor

The sequence of events described above occurs at any given spot in a CVD flow reactor. As an example, one can consider the deposition of tungsten on the interior wall of a graphite tube by the hydrogen reduction of the fluoride as follows:



As shown schematically in Fig. 2.4a, the reactant gases are introduced in the upstream side, then flow down the reactor tube, and exhaust downstream through the vacuum pump.

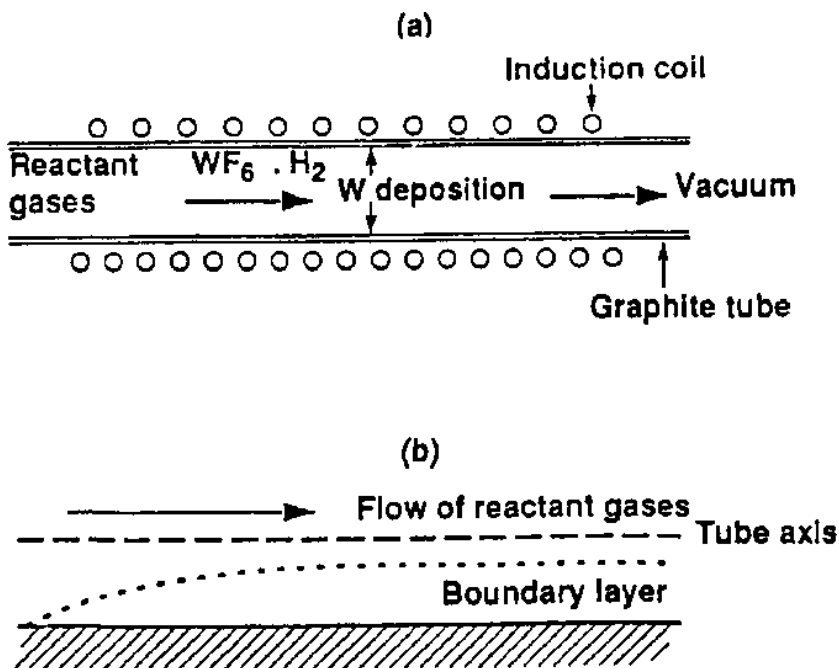


Figure 2.4. (a) Tungsten deposition in a tubular reactor, (b) boundary layer conditions.

3.3 Boundary Layer

The behavior of the gas as it flows down the tube is controlled by fluid mechanics and a complete investigation would be lengthy and outside the scope of this book. It is enough to say that the Reynolds number, R_e , which is a dimensionless parameter that characterizes the flow of a fluid, is such that the gas flow is generally laminar, although in some instances the laminar flow may be disturbed by convective-gas motion and may become turbulent.

In the case of laminar flow, the velocity of the gas at the deposition surface (the inner wall of the tube) is zero. The boundary is that region in which the flow velocity changes from zero at the wall to essentially that of the bulk gas away from the wall. This boundary layer starts at the inlet of the tube and increases in thickness until the flow becomes stabilized as shown in Fig. 2.4b. The reactant gases flowing above the boundary layer have to diffuse through this layer to reach the deposition surface as is shown in Fig. 2.3.

The thickness of the boundary layer, Δ , is inversely proportional to the square root of the Reynolds number as follows:

$$\text{Eq. (4)} \quad \Delta = \sqrt{\frac{x}{R_e}}$$

$$\text{where: } R_e = \frac{\rho u_x}{\mu}$$

ρ = mass density

u = flow density

x = distance from inlet in flow direction

μ = viscosity

This means that the thickness of the boundary layer increases with lower gas-flow velocity and with increased distance from the tube inlet.^[14]

3.4 Gas Velocity

Under such conditions, it is possible to obtain an approximate visualization of the gas-flow pattern by using TiO_2 smoke (generated when titanium chloride comes in contact with moist air), although thermal diffusion may keep the smoke particles away from the hot surface where a steep temperature gradient exists. Figure 2.5 shows a typical velocity pattern in a horizontal tube. As mentioned above, a steep velocity gradient is noticeable going from maximum velocity at the center of the tube to zero velocity at the surface of the wall. The gradient is also shallow at the entrance of the tube and increases gradually toward downstream.

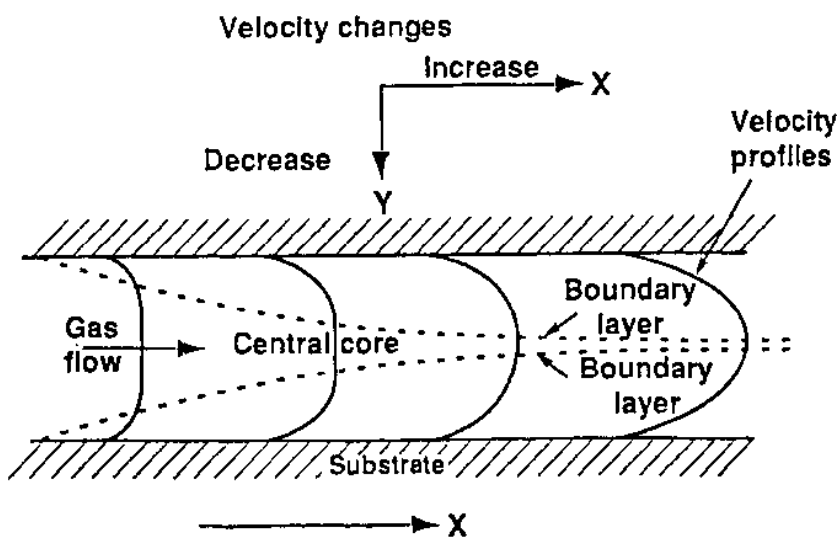


Figure 2.5. Boundary layer and velocity changes in a tube reactor, showing the graphs of velocity recorded at different positions on the tube.

3.5 Temperature

Figure 2.6 shows a typical temperature profile.^[2] The temperature boundary layer is similar to the velocity layer. The flowing gases heat rapidly as they come in contact with the hot surface of the tube, resulting in a steep temperature gradient. The average temperature increases toward downstream.

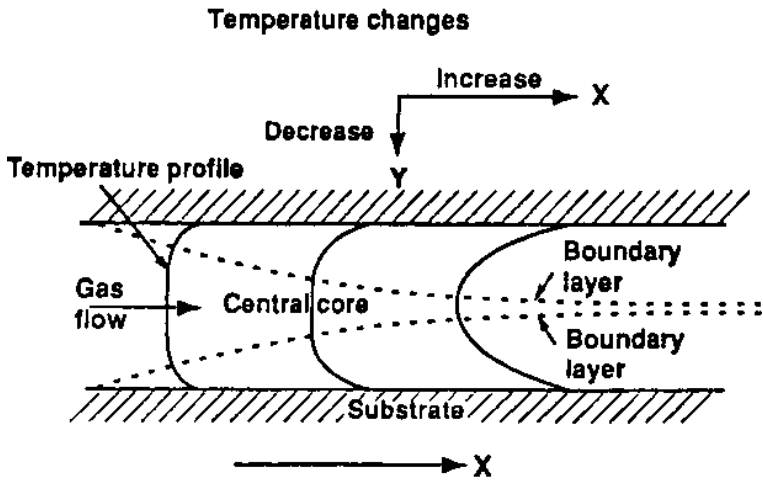


Figure 2.6. Temperature boundary layer and temperature changes in a tubular reactor, showing the graphs of temperature recorded at different positions on the tube.

3.6 Reactant-Gas Concentration

As the gases flow down the tube, they become gradually depleted as tungsten is deposited and the amount of the by-product gas, HF, increases in the boundary layer. This means that, at some point downstream, deposition will cease altogether when WF_6 is no longer present. The reactant concentration is illustrated in Fig. 2.7.

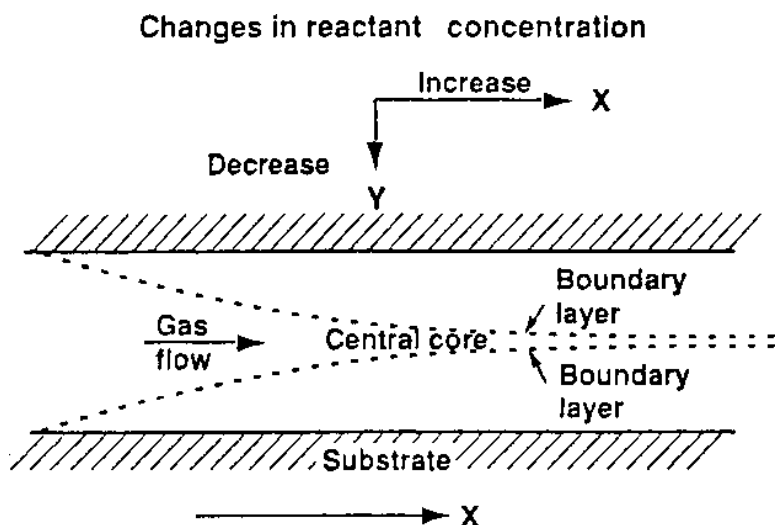


Figure 2.7. Changes in reactant concentration in a tubular reactor.

The boundary layers for these three variables (gas velocity, temperature, and concentration) may sometimes coincide, although in slow reactions, the profiles of velocity and temperature may be fully developed at an early stage while the deposition reaction is spread far downstream the tube.

As can be seen, conditions in a flowing reactor, even the simplest such as a tube, may be far from the thermodynamic equilibrium conditions predicted by the equilibrium computer programs. However, in the diffusion controlled range, it is possible to use as the driving force for diffusion, the difference between an assumed equi-

librium composition at the wall and the bulk-gas composition in the feed (adjusted for downstream depletion), to model some systems to a first approximation.

3.7 Rate-Limiting Steps

What is the rate limiting step of a CVD reaction? In other words, what factor controls the growth rate of the deposit? The answer to this question is critical since it will help to optimize the deposition reaction, obtain the fastest growth rate and, to some degree, control the nature of the deposit.

The rate-limiting step is generally determined by either the surface reaction kinetics or by mass transport.

3.8 Surface-Reaction Kinetics

In the case of control by surface reaction kinetics, the rate is dependent on the amount of reactant gases available. As an example, one can visualize a CVD system where the temperature and the pressure are low. This means that the reaction occurs slowly because of the low temperature and there is a surplus of reactants at the surface since, because of the low pressure, the boundary layer is thin, the diffusion coefficients are large, and the reactants reach the deposition surface with ease as shown in Fig. 2.8a.

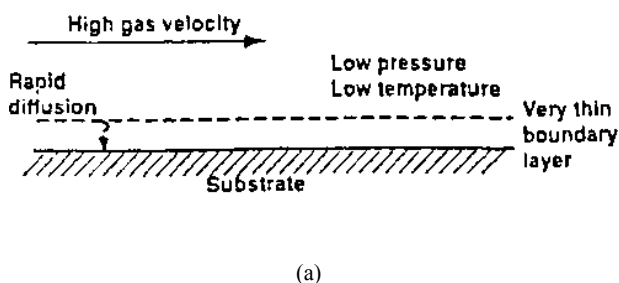
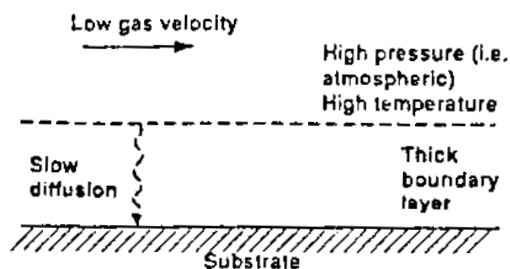


Figure 2.8. Rate-limiting steps in a CVD reaction (a) surface reaction kinetics control, (b) diffusion control.



(b)

Figure 2.8. (*Cont'd.*)

3.9 Mass Transport

When the process is limited by mass-transport phenomena, the controlling factors are the diffusion rate of the reactant through the boundary layer and the diffusion out through this layer of the gaseous by-products. This usually happens when pressure and temperature are high. As a result, the gas velocity is low as was shown above, and the boundary layer is thicker making it more difficult for the reactants to reach the deposition surface. Furthermore, the decomposition reaction occurs more rapidly since the temperature is higher and any molecule that reaches the surface reacts instantly. The diffusion rate through the boundary layer then becomes the rate limiting step as shown in Fig. 2.8b.

3.10 Control of Limiting Step

To summarize, the surface kinetics (or near surface kinetics) is the limiting step at lower temperature and diffusion is the rate limiting step at higher temperature. It is possible to switch from one rate-limiting step to the other by changing the temperature. This is illustrated in Fig. 2.9, where the Arrhenius plot (logarithm of the deposition rate vs. the reciprocal temperature) is shown for several reactions leading to the deposition of silicon,

using either SiH_4 , SiH_2Cl_2 , SiHCl_3 , or SiCl_4 as silicon sources in a hydrogen atmosphere.^[15]

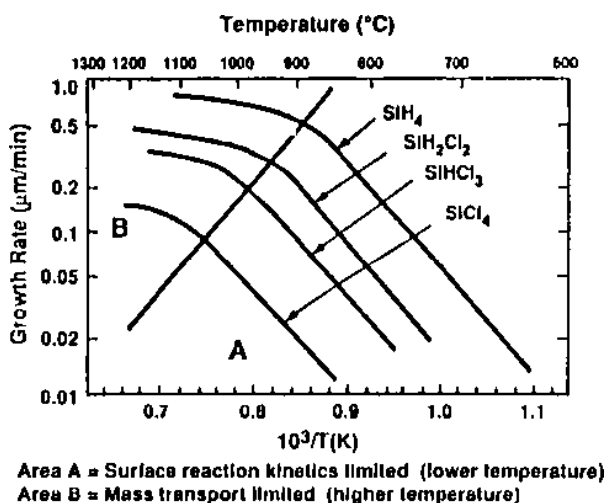


Figure 2.9. Arrhenius plot for silicon deposition using various precursors.

In the A sector (lower right), the deposition is controlled by surface-reaction kinetics as the rate-limiting step. In the B sector (upper left), the deposition is controlled by the mass-transport process and the growth rate is related linearly to the partial pressure of the silicon reactant in the carrier gas. Transition from one rate-control regime to the other is not sharp, but involves a transition zone where both are significant. The presence of a maximum in the curves in Area B would indicate the onset of gas-phase precipitation, where the substrate has become starved and the deposition rate decreased.

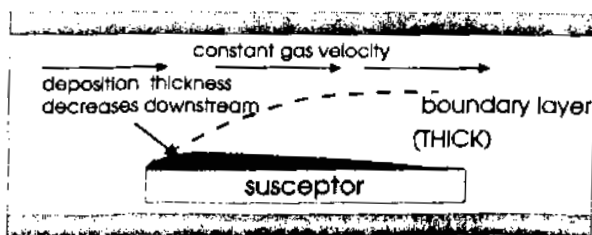
3.11 Pressure as Rate-Limiting Factor

Pressure is similar to temperature as a rate limiting factor since the diffusibility of a gas is inversely related to its pressure. For instance, lowering the pressure 760 Torr (1 atm) to 1 Torr increases the gas-phase transfer of reactants to the deposition surface and the

diffusion out of the by-products by more than 100 times. Clearly, at low pressure, the effect of mass-transfer variables is far less critical than at higher pressure.

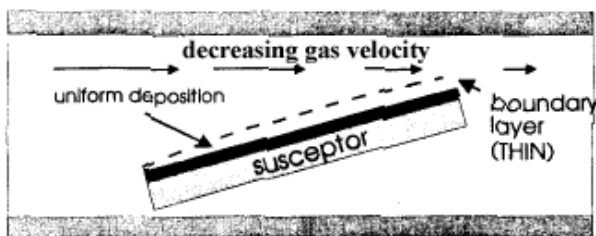
However, the gain may not be as large if the overall pressure decrease is at the expense of the partial pressure of reactant gas, since the kinetic rate (for first-order reactions) is proportional to the partial pressure of the reactant. Reducing the pressure by reducing the flow of carrier gas (or eliminating altogether) is a good alternative and is usually beneficial. At low pressure, surface reaction is the rate determining step and the mass-transfer variables are far less critical than at atmospheric pressure.

It can be now seen that, by proper manipulation of the process parameters and reactor geometry, it is possible to control the reaction and the deposition to a great degree. This is illustrated by the following example. In the deposition of tungsten in a tube mentioned in Sec. 3.2 above, the gas velocity is essentially constant and the boundary layer gradually increases in thickness toward downstream. This means that the thickness of the deposit will decrease as the distance from the tube inlet increases, as shown in Fig. 2.10a. This thickness decrease can be offset and a more constant thickness obtained simply by tilting the susceptor, as shown in Fig. 2.10b. This increases the gas velocity due the flow constriction; the Reynolds number goes up; the boundary layer decreases and the deposition rate is more uniform.^[14]



(a)

Figure 2.10. Control of deposition uniformity in a tubular reactor (a) susceptor parallel to gas flow, (b) tilted susceptor.



(b)

Figure 2.10. (Cont'd.)

3.12 Mathematical Expressions of the Kinetics of CVD

The flow-dynamics and mass-transport processes can be expressed mathematically and realistic models obtained to be used in the predictions of a CVD operation and in the design of reactors.^{[16]–[18]} These models are designed to define the complex entrance effects and convection phenomena that occur in a reactor and solve the complete equations of heat, mass balance, and momentum. They can be used to optimize the design parameters of a CVD reactor such as susceptor geometry, tilt angle, flow rates, and others. To obtain a complete and thorough analysis, these models should be complemented with experimental observations, such as the flow patterns mentioned above and in situ diagnostic, such as laser Raman spectroscopy.^[19]

4.0 GROWTH MECHANISM AND STRUCTURE OF DEPOSIT

In the previous sections, it was shown how thermodynamic and kinetic considerations govern a CVD reaction. In this section, the nature of the deposit, i.e., its microstructure and how it is controlled by the deposition conditions, is examined.

4.1 Deposition Mechanism and Epitaxy

The manner in which a film is formed on a surface by CVD is still a matter of controversy and several theories have been advanced to describe the phenomena.^[2] A thermodynamic theory proposes that a solid nucleus is formed from supersaturated vapor as a result of the difference between the surface free energy and the bulk free energy of the nucleus. Another and newer theory is based on atomistic nucleation and combines chemical bonding of solid surfaces and statistical mechanics.^[20] These theories are certainly valuable in themselves but considered outside the scope of this book.

There are, however, three important factors that control the nature and properties of the deposit to some degree which must be reviewed at this time: epitaxy, gas-phase precipitation, and thermal expansion.

4.2 Epitaxy

The nature of the deposit and the rate of nucleation at the very beginning of the deposition are affected, among other factors, by the nature of the substrate. A specific case is that of epitaxy where the structure of the substrate essentially controls the structure of the deposit.^{[2][15][20]} Epitaxy can be defined as the growth of a crystalline film on a crystalline substrate, with the substrate acting as a seed crystal. When both substrate and deposit are of the same material (for instance silicon on silicon) or when their crystalline structures (lattice parameters) are identical or close, the phenomena is known as homoepitaxy. When the lattice parameters are different, it is heteroepitaxy. Epitaxial growth cannot occur if these structural differences are too great.

A schematic of epitaxial growth is shown in Fig. 2.11. As an example, it is possible to grow gallium arsenide epitaxially on silicon since the lattice parameters of the two materials are similar. On the other hand, deposition of indium phosphide on silicon is not possible since the lattice mismatch is 8%, which is too high. A solution is to use an intermediate buffer layer of gallium arsenide between the silicon and the indium phosphide. The lattice parameters of common semiconductor materials are shown in Fig. 2.12.

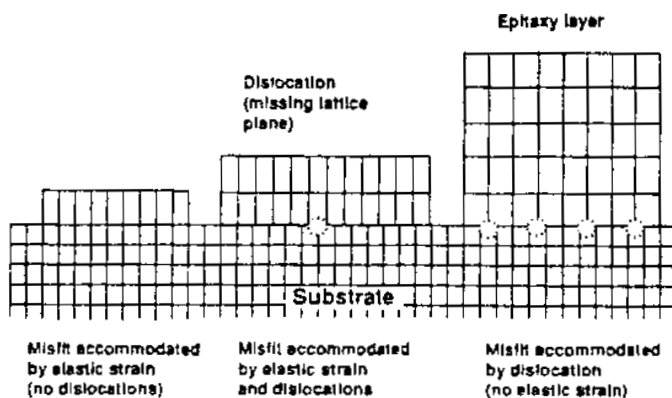


Figure 2.11. Epitaxy accommodations of lattice mismatch.

Generally, epitaxial films have superior properties and, whenever possible, epitaxial growth should be promoted. The epitaxial CVD of silicon and III–V and II–VI compounds is now a major process in the semiconductor industry and is expected to play an increasingly important part in improving the performance of semiconductor and optoelectronic designs (see Chs. 13–15).^[22]

4.3 Gas Phase Precipitation

As mentioned previously, a CVD reaction may occur in the gas phase instead of at the substrate surface if the supersaturation of the reactive gases and the temperature are sufficiently high. This is generally detrimental because gas-phase precipitated particles, in the form of soot, become incorporated in the deposit, causing nonuniformity in the structure, surface roughness, and poor adhesion. In some cases, gas-phase precipitation is used purposely, such as in the production of extremely fine powders (see Ch. 19).

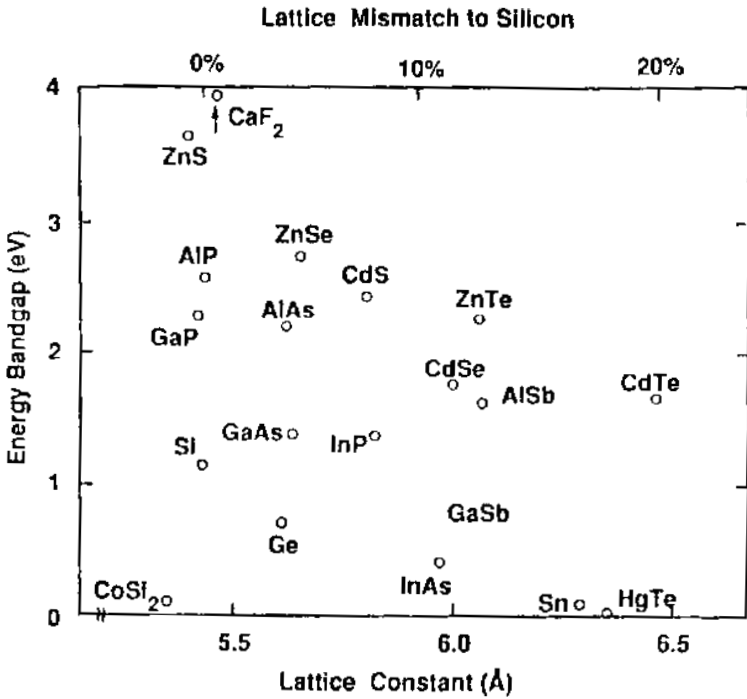


Figure 2.12. Bandgap and lattice constant of semiconductor materials.

4.4 Thermal Expansion

Large stresses can be generated in a CVD coating during the cooling period from deposition temperature to room temperature, if there is a substantial difference between the coefficient of thermal expansion (CTE) of the deposit and that of the substrate. These stresses may cause cracking and spalling of the coating. If differences are large, it may be necessary to use a buffer coating with an intermediate CTE or with high ductility. Deposition processes which

do not require high temperatures, such as MOCVD or plasma CVD, should also be considered (see Ch. 4 and 5). Table 2.1 lists the CTE of typical CVD materials and substrates.

4.5 Structure and Morphology of CVD Materials

The properties of a CVD material are directly related to the nature of its structure which is in turn controlled by the deposition conditions. In this section and the next, the relationship between properties, structure, and deposition conditions is examined.

The structure of a CVD material can be classified into three major types which are shown schematically in Fig. 2.13.^[23] In Zone (A), the structure consists of columnar grains which are capped by a domelike top. In Zone (B), the structure is also columnar but more faceted and angular. In Zone (C), it consists of fine accost grains. Examples of these structures are shown in Fig. 2.14.^[24] This is the CVD equivalent of the structural model for vacuum-evaporated films first introduced by Movchan and Demshishin.^[25]

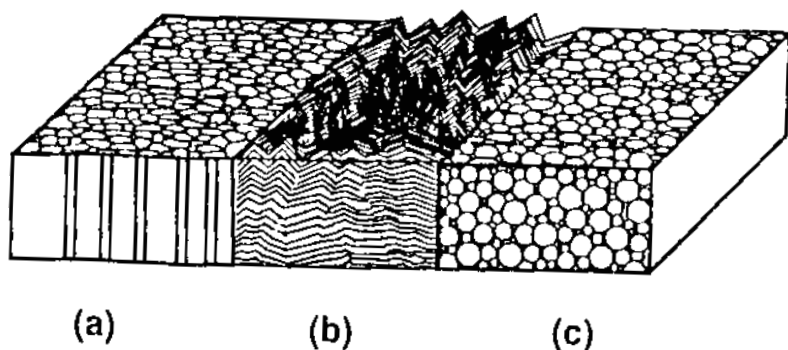
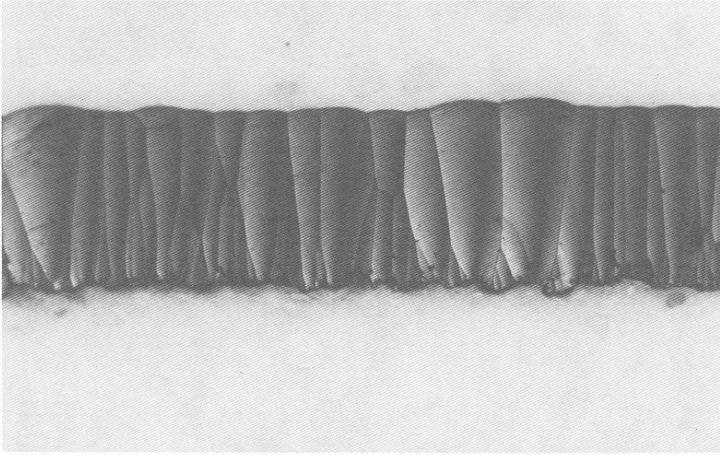


Figure 2.13. Schematic of structures obtained by CVD: (a) columnar grains with domed tops, (b) faceted columnar grains, (c) equiaxed fine grains.

Table 2.1
Coefficient of Thermal Expansion (CTE) of Typical CVD Materials
and Substrates

Materials	CTE (ppm/°C) 25–300°C
Metals	
Aluminum	23.5
Gold	14.2
Iridium	6
Molybdenum	5
Niobium	7
Steel (carbon)	12
Stainless Steel (302)	17.3
Tantalum	6.5
Titanium	9
Tungsten	4.5
Non Metallic Elements	
Carbon, hot-pressed	5.4
Carbon-carbon	0.5
Silicon	3.8
Ceramics	
Alumina	8.3
Boron carbide	4.5
Boron nitride	7.5
Chromia	8
Hafnia	7
Magnesia	13
Molybdenum disilicide	8.25
Silicon carbide	3.9
Silicon nitride	2.45
Silicon oxide	0.5
Titanium carbide	7.6
Titanium diboride	6.6
Titanium nitride	9.5
Tungsten carbide	4.5
Tungsten disilicide	6.6

Note: Reported values of CTE's often vary widely. The values listed here are an average from several sources.

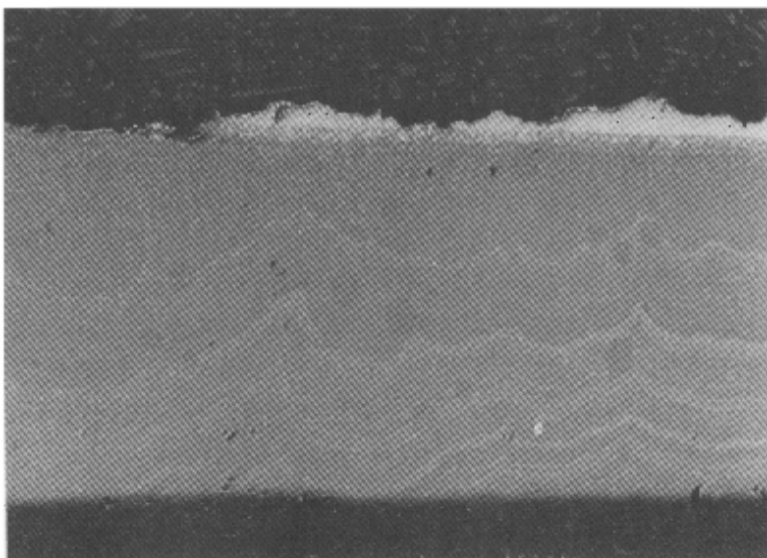


(a)

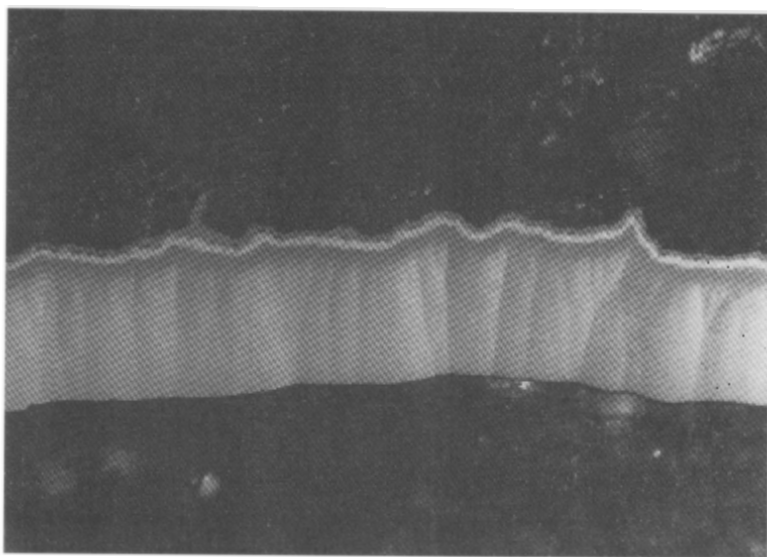


(b)

Figure 2.14. Examples of CVD structures: (a) columnar grains with domed tops, (b) faceted columnar grains, (c) equiaxed fine grains, (d) mixed structures. (Source: *Ultramet, Pacoima, CA.*)



(c)



(d)

Figure 2.14. (*Cont'd.*)

As might be expected, the microstructure varies depending on the material being deposited. In general, ceramics obtained by CVD such as SiO_2 , Al_2O_3 , Si_3N_4 , and most dielectric materials tend to be amorphous or, at least, have a very small grain microstructure (Type C). Metal deposits tend to be more crystalline with the typical columnar structure of type (A) or (B). The crystal size of the deposits is also a function of deposition conditions, especially temperature. Generally, the most desirable structure for load-bearing use is the fine accost (C), which usually has the highest mechanical properties, such as hardness and fracture toughness.

More often than not, a deposited structure will include two and sometimes all three types. This usually happens in thick deposits where a uniform structure is more difficult to obtain.

4.6 Control of CVD Microstructure

It is possible to control the nature of a CVD structure by the proper manipulation of the deposition parameters such as temperature, pressure, supersaturation, and the selection of the CVD reaction.

Pressure controls the thickness of the boundary layer and consequently the degree of diffusion as was shown above. By operating at low pressure, the diffusion process can be minimized and surface kinetics becomes rate controlling. Under these conditions, deposited structures tend to be fine-grained, which is usually a desirable condition (Fig. 2.13c). Fine-grained structures can also be obtained at low temperature and high supersaturation as well as low pressure.

At higher temperatures, deposits tend to be columnar (Fig. 2.13 a and b) as a result of uninterrupted grain growth toward the reactant source. The structure is also often dependent on the thickness of the deposit. For instance, grain size will increase as the thickness increases. A columnar-grain structure develops, which becomes more pronounced as the film becomes thicker.

Columnar structures are usually undesirable as the deleterious effects of grain growth and columnar formation can be considerable. They may lead to structural, chemical, and electrical anisotropy and the rapid diffusion of impurities along the grain boundaries. It is possible to reduce or eliminate columnar deposits and obtain fine-grain accost growth by mechanical means such as rubbing or brushing at regular intervals to renucleate the deposition surface. This approach has been demonstrated in the deposition of tungsten.^[13] However, it is not generally practical, particularly when substrates of complex geometry are used.

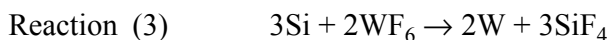
Another approach is the control of grain growth by chemical means.^{[26][27]} In the deposition of tungsten for instance, a fine-grain equiaxial growth is obtained by depositing alternating layers of tungsten and silicon. Typically a layer of tungsten, approximately 100 nm thick, is deposited using the hydrogen reduction of WF_6 at 550°C and a pressure of a few Torr as follows:



A 15 nm thick layer of silicon is then deposited by the thermal decomposition of silane at the same temperature and pressure as follows:



WF_6 is then reintroduced in the system and the thin layer of silicon is reduced as follows:



After the silicon is completely reduced, Reaction (3) stops and Reaction (1) is resumed. The temporary deposition of sacrificial silicon interrupts the tungsten grain growth as new nucleation sites are created. Larger grain and columnar growth are essentially eliminated

and a fine-grain structure is the result. A similar process can be used for the deposition of rhenium and other metals.

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3

The Chemistry of CVD

1.0 CATEGORIES OF CVD REACTIONS

Before any CVD program is undertaken, it is essential to evaluate all the potential reactions and select the most appropriate. This is done by a thermodynamic analysis as described in Ch. 2 and, if necessary, by an experimental program.

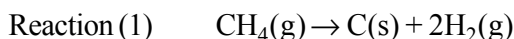
The CVD reactions can be classified in several major categories which are outlined below. These reactions and others are described in greater detail in Chs. 6–11 where the materials produced by CVD are reviewed.

Metallo-organic CVD (MOCVD) is major area of CVD which is rapidly growing, particularly in semiconductor and optoelectronic applications. It is treated separately in Ch. 4.

1.1 Thermal-Decomposition (or Pyrolysis) Reactions

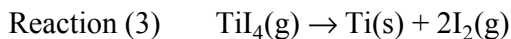
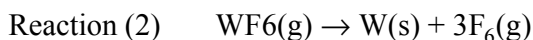
In thermal-decomposition reactions, a molecule is split into its elements and/or a more elementary molecule. Such reactions are the simplest since only one precursor gas is required. Typical examples are as follows:

Hydrocarbon Decomposition

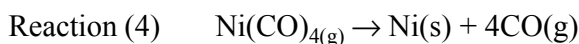


This reaction is used extensively in the production of carbon, graphite and diamond.

Halide Decomposition (See Sec. 3 Below)

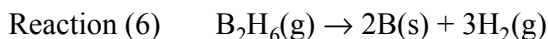
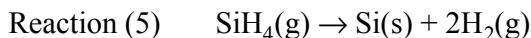


Carbonyl Decomposition (See Sec. 4 Below)



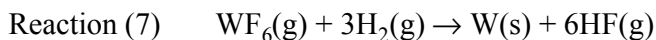
This also includes the decomposition of the more complex carbonyls such as the carbonyl hydrides and nitrosylcarbonyls.

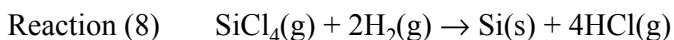
Hydride Decomposition (See Sec. 5 Below)



1.2 Hydrogen Reduction

Reduction is a chemical reaction in which an element gains an electron, in other words, when the oxidation state is lowered.^[1] Reduction reactions are widely used, particularly the hydrogen reduction of the halides, as shown in the following examples:





These two reactions are actually simplified versions and several intermediate reactions generally occur with the formation of lower halides.

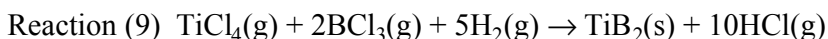
Hydrogen reduction has a major advantage in that the reaction generally takes place at lower temperature than the equivalent decomposition reaction. It is used extensively in the deposition of transition metals from their halides, particularly the metals of Groups Va, (vanadium, niobium, and tantalum) and VIa (chromium, molybdenum, and tungsten). The halide reduction of Group IVa metals (titanium, zirconium, and hafnium) is more difficult because their halides are more stable.

The hydrogen reduction of the halides of nonmetallic elements, such as silicon (Reaction 8) and boron, is an essential process in the production of semiconductors and high-strength fibers.

Note: Hydrogen is used in a supplementary role in reactions where reduction is not the primary function, for instance where it is necessary to prevent the formation of oxides or carbides and generally improve the characteristics and properties of the deposited material.

1.3 Coreduction

The deposition of a binary compound can be achieved by a coreduction reaction. In this manner, ceramic materials such as oxides, carbides, nitrides, borides, and silicides can be produced readily and usually more readily than the parent metal. A common example is the deposition of titanium diboride:



1.4 Metal Reduction of the Halides

Although hydrogen is the most common reductant, there are other elements which are more powerful, such as zinc, cadmium, magnesium, sodium, and potassium, as shown in Table 3.1.

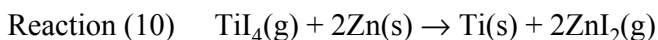
Table 3.1

Free Energy of Formation of Reductant Elements^[2]

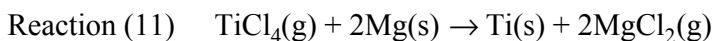
Reductant	Melt Point °C	Boil Point °C	Chloride	Standard Free Energy of Formation (KJoule per mole) at the given temperatures (°C)			
				425	725	1025	1325
H ₂			HCl	-98	-100	-102	-104
Cd	320	765	CdCl ₂	-264	-241	-192	-164
Zn	419	906	ZnCl ₂	-307	-264	-262	-254
Mg	650	1107	MgCl ₂	-528	-482	-435	-368
Na	97	892	NaCl	-223	-238	-241	229
K	631	760	KCl	-369	-341	-295	

In this table, the free energy of formation, ΔG_f° , of the chloride of these metals is listed for four different temperatures. As can be seen, the values are more negative than that of hydrogen chloride. These metals can be used to reduce the halides of titanium, zirconium, or hafnium, whereas hydrogen, as mentioned above, cannot do so readily. In order to be useful in CVD, the by-product chloride must be volatile at the deposition temperature. This may rule out the use of sodium or potassium, which evaporate above 1400°C.

Of these reductant metals, the most commonly used is zinc. The reason is that the zinc halides are more volatile than the parent metal and the chances of codeposition of the halides are minimized. Either chloride or iodide is used, although the iodide, being the most volatile, is usually preferred. The volatility of these halides decreases as one goes from the iodides to the chlorides to the fluorides. The reaction is as follows:



Another reductant, magnesium, is used in the industrial production of titanium metal as follows:

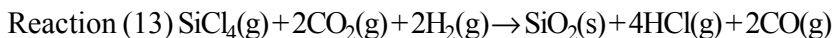
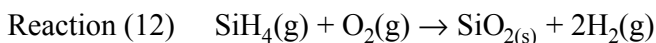


The alkali metals, sodium and potassium, shown in Table 3.1 are not generally used as reductant because their reductive power is so high that it tends to cause premature and detrimental gas-phase precipitation and, as mentioned above, high temperature is necessary to volatilize these metals.

1.5 Oxidation and Hydrolysis Reactions

Oxidation and hydrolysis are two important groups of CVD reactions which are used in the formation of oxides. Common sources of oxygen are the element itself and CO_2 . Recently, ozone (O_3) has been used for the deposition of SiO_2 .^{[3][4]} It is a powerful oxidizing agent which is often generated *in situ*, by a corona discharge in oxygen.

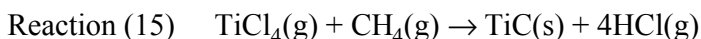
Typical oxidation and hydrolysis reactions are:





1.6 Carbidization and Nitridation

The deposition of carbides (carbidization) is usually obtained by reacting a halide with a hydrocarbon, such as methane, as follows:



The deposition of nitrides (nitridation or ammonolysis) is generally based on ammonia which is preferred to nitrogen. Ammonia has a positive free energy of formation; thus its equilibrium products are essentially hydrogen and nitrogen which become the reactants for the CVD reaction. The observed advantage of ammonia as a reactant lies in the kinetics of the nascent hydrogen and nitrogen atoms from the ammonia decomposition. Thermodynamically, the reaction of 2NH_3 and of N_2 and H_2 are equivalent.

An example of the use of ammonia is the deposition of silicon nitride, a common reaction in the semiconductor industry:^[5]



2.0 CVD PRECURSORS

In the previous section, the general categories of CVD reactions were reviewed and, as can be readily seen, the choice of the proper reactants (the precursors) is very important. These precursors fall into several general groups which are the halides, carbonyls and hydrides (the metallo-organics are reviewed in Ch. 4). A general review of the nature and properties of these precursors is given in this section which should help in making the proper precursor selection and gaining a better understanding of the CVD reactions.

The choice of a precursor is governed by certain general characteristics which can be summarized as follows:

- Stability at room temperature.
- Ability to react cleanly in the reaction zone.
- Sufficient volatility at low temperature so that it can be easily transported to the reaction zone without condensing in the lines.
- Capability of being produced in a very high degree of purity.
- Ability to react without producing side reactions or parasitic reactions.

3.0 HALIDE PRECURSORS

The halides are binary compounds of a halogen (elements of group VIIb of the periodic table) and a more electropositive element such as a metal.

3.1 Halogens

The halogens include fluorine, chlorine, bromine and iodine and all have been used in CVD reactions. They are reactive elements and exist as diatomic molecules, i.e., F_2 , Cl_2 , etc. Their relevant properties are listed in Table 3.2.

Of all the elements, fluorine is the most chemically reactive. It combines directly with other elements. Chlorine is slightly less reactive. Both are gases at room temperature which is an important advantage in delivery and metering. Because of their reactivity, they form halides readily, but also attack most materials which makes them difficult to handle and requires equipment designed with inert materials such as Monel or Teflon. Halogens are also toxic, fluorine more so than chlorine by an order of magnitude.

Table 3.2
Relevant Properties of the Halogens^[6]

Element	Electron Affinity KJ g-atom	Boiling Point °C	Melting Point °C
Fluorine	339	-118	-233
Chlorine	355	-34.6	-103
Bromine	331	58.7	-7.2
Iodine	302	184.3	113.5

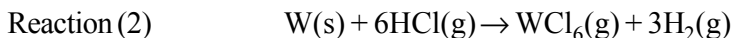
Bromine is a dark-red liquid with high specific gravity. Iodine is a black solid which sublimes at atmospheric pressure producing a violet vapor. Both are used in CVD but to a lesser degree than either fluorine or chlorine.

3.2 Halide Formation or Halogenation

Halides can be formed by the direct interaction of the halogen as follows:



or by the reaction with another halide such as hydrogen chloride:



Reaction (2) is often preferred because of the hazard of unconsumed chlorine from Reaction (1) reacting explosively with hydrogen commonly used as a reducing agent.

3.3 Halide Properties

Properties of some halides useful in CVD are listed in Table 3.3. As can be seen, some of these halides are gaseous or liquid at room temperature and, as such, are easily transported in the reaction chamber. The solid halides, however, must be heated to produce sufficient vapor. This sometimes presents a problem which can be bypassed by generating the halide *in situ* (see Ch. 5). Most halides are available commercially.

Table 3.3
Properties of Selected Halides^[6]

Halides	Melting Point °C	Boiling Point °C
AlBr ₃	97.5	263
AlCl ₃	190	182.7 (s)
BCl ₃	-107.3	12.5
BF ₃	126.7	-99.9
CCl ₄	-23	76.8
CF ₄	-184	-128
CrCl ₂	824	1300 (s)
HfCl ₄	319	319 (s)
HfI ₄		400 (s)
MoCl ₅	194	268
MoF ₆	17.5	35
NbCl ₅	204.7	254
ReF ₆	18.8	47.6
SiCl ₄	-70	57.6
TaBr ₅	265	348.8
TaCl ₅	216	242
TiCl ₄	-25	136
VCl ₄	-28	148.5
WCl ₅	248	275.6
WF ₆	2.5	17.5
ZrBr ₄	450	357 (s)
ZrCl ₄	437	331 (s)
Note: (s) indicates that the compound sublimates at atmospheric pressure before melting.		

4.0 METAL-CARBONYL PRECURSORS

Metal carbonyls form a large and important group of compounds which are used widely in the chemical industry, particularly in the preparation of heterogeneous catalysts and as precursors in CVD and metallo-organic CVD (MOCVD).

4.1 Characteristics of the Carbonyls

The carbonyls are relatively simple compounds since they consist of only two components:

- The carbonyl group which is a functional group where a carbon atom is doubly bonded to an oxygen atom(CO) .
- A d-group transition metal.

The atomic structure of the transition metals is such that the *d* shell is only partly filled. The first transition series (3d) comprises Sc, Ti, V, Cr, Mn, Fe, Co, and Ni; the second (4d), Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag; the third (5d), Hf, Ta, W, Re, Os, Ir, Pt, and Au. Carbonyl derivatives of at least one type are found for all these metals. Although only a few are presently used in CVD, many are being investigated as they constitute an interesting and potentially valuable group of precursor materials.

The simplest transition metal carbonyls are mononuclear of the type $M(CO)_x$, in other words those with only one metal atom. They are hydrophobic but soluble to some extent in nonpolar liquids, such as n-butane or propane. The dinuclear carbonyls are more complex but have the same general characteristics as the mononuclear carbonyls. The carbonyls, which are or could be used in CVD, are listed in Table 3.4 with some of their properties.

More complex yet are the polynuclear or cluster carbonyls, some of which are used as CVD precursors such as: $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$.

Table 3.4
Selected Properties of Metal Carbonyls^{[1][7]}

Compound	MP °C	BP °C	Sp.Gr.	Color & Form	Structure	Comments
MONONUCLEAR						
V(CO) ₆	65	dec.		Black crystal	Octahedral	Yellow-orange in solution, volatile, very unstable
Cr(CO) ₆	164	dec. 180	1.77	White crystal	Octahedral	Volatile
Fe(CO) ₅	-20	103	1.42	Yellow liquid		Poisonous
Ni(CO) ₄	-25	43	1.32	Colorless liquid		Very toxic
Mo(CO) ₆	150	dec. 180		White crystal	Octahedral	Volatile
Ru(CO) ₅	-22			Colorless liquid		Very volatile
W(CO) ₆	169	dec. 180	2.65	White crystal	Octahedral	Volatile
Os(CO) ₅	-15			Colorless liquid		Very volatile
DINUCLEAR						
Mn ₂ (CO) ₁₀	152			Crystal		
Fe ₂ (CO) ₉	80 dec.	2.08		Yellow crystal	Hexagonal	Volatile
Co ₂ (CO) ₈	51	52 dec.	1.73	Orange crystal		CO loss
Re ₂ (CO) ₁₀	170	250 dec.		Colorless crystal		Cubic Volatile
Ir ₂ (CO) ₈	160			Yellow crystal		Sublimes in CO ₂ at 160°C

4.2 Carbonyl Preparation

Many metal carbonyls are available commercially. However, in some cases, the CVD investigator may find it more expedient (and sometimes cheaper) to produce them in-house. This is particularly true of the only two carbonyls that can be obtained by the direct reaction of the metal with CO (and consequently easy to synthesize), i.e., nickel carbonyl, $\text{Ni}(\text{CO})_4$, and iron carbonyl, $\text{Fe}(\text{CO})_5$.

Table 3.5 summarizes the various synthesis processes.

Table 3.5
Metal Carbonyl Preparation

Carbonyl	Process
$\text{Ni}(\text{CO})_4$	Direct reaction with CO at one atm and at 80°C
$\text{Fe}(\text{CO})_5$	Direct reaction with CO at one atm and at 150–300°C
$\text{Co}_2(\text{CO})_8$	Reaction of the carbonate with CO at 250–300 atm and at 120–200°C
$\text{V}(\text{CO})_6$ $\text{Cr}(\text{CO})_6$ $\text{W}(\text{CO})_6$ $\text{Re}_2(\text{CO})_{10}$	Reaction of the chloride with CO with a reducing agent at 200–300 atm and at 300°C
$\text{Os}(\text{CO})_5$ $\text{Re}_2(\text{CO})_{10}$	Reaction of the oxide with CO at 300°C
$\text{Ru}_3(\text{CO})_{12}$	Reaction of acetylacetonate with CO at 150°C and 200 atm

4.3 Metal Carbonyl Complexes

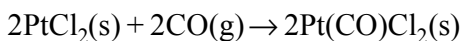
Metal carbonyls form several complexes but those of major interest in MOCVD are the carbonyl halides and the carbonyl-nitric-oxide complexes.

The carbonyl halides have the general formula $M_x(\text{CO})_yX_z$ with X being fluorine, chlorine, bromine, or iodine. With the notable exception of nickel, most metals form carbonyl halides including all the metals listed in Table 3.4.

A particularly interesting case is that of the platinum metal group which, in addition to platinum (Pt), comprises ruthenium (Ru), osmium (Os), rhodium (Rh), iridium (Ir), and palladium (Pd). These carbonyl halides are usually the most practical precursors for metal deposition because of their high volatility at low temperature. Indeed two of them, palladium and platinum, do not form carbonyls but only carbonyl halides. So does gold.

The hydrogen reduction of the metal halides, described in Sec. 1.2, is generally the favored reaction for metal deposition but is not suitable for the platinum-group metals since the volatilization and decomposition temperatures of their halides are too close to provide efficient vapor transport.^[2] For that reason, the decomposition of the carbonyl halide is preferred. The exception is palladium which is much more readily deposited by hydrogen reduction than by the carbonyl-halide decomposition.

Preparation of Carbonyl Halides. The carbonyl halides are generally produced by the direct reaction of the metal halide and CO, usually at high pressure and at the temperature range of 140–290°C. A typical reaction is:^[8]



Some examples of carbonyl halides are shown in Table 3.6.

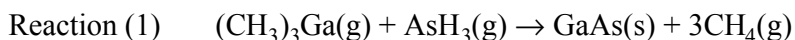
Carbonyl Nitric Oxides. Another group of metal-carbonyl complexes, worthy of investigation as CVD precursors, consists of the carbonyl nitric oxides. In these complexes, one (or more) CO group is replaced by NO. An example is cobalt nitrosyl tricarbonyl, $\text{CoNO}(\text{CO})_3$, which is a preferred precursor for the CVD of cobalt. It is a liquid with a boiling point of 78.6°C which decomposes at 66°C. It is prepared by passing NO through an aqueous solution of cobalt nitrate and potassium cyanide and potassium hydroxide.^[9]

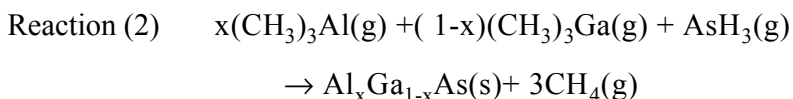
Table 3.6
Metal Carbonyl Halides^[1]

Compound	MP°C	BP°C	Sp.Gr.	Color & Form	Comments
Mn(CO) ₅ Cl				Yellow crystal	Loses CO at 120°C in organic solvent
Re(CO) ₄ Cl ₂		250 dec.		White crystal	
Ru(CO) ₂ I ₂				Orange powder	Suitable for CVD
Os(CO) ₃ Cl ₂	270	280 dec.		Colorless prism	Suitable for CVD
RhCl ₂ RhO(CO) ₃	125	subl.		Ruby red needle cr.	Suitable for CVD
Ir(CO) ₂ Cl ₂	140 dec.			Colorless needle cr.	Suitable for CVD
Pt(CO)Cl ₂	195	300 dec.	4.23	Yellow needle cr.	Sublimes in CO ₂ at 240°C Suitable for CVD
Pt(CO) ₂ Cl ₂	142	210	3.48	Light yel. needle cr.	Sublimes in CO ₂ at 210°C

5.0 HYDRIDE PRECURSORS

Hydrides are an important group of precursors that are used to deposit single elements such as boron or silicon. As described in Ch. 4, they are also used in conjunction with metallo-organics to form III–V and II–VI semiconductor compounds as shown in the following examples:^[10]





Many elements form hydrides but only few hydrides are presently used as CVD precursors. These are the hydrides of elements of groups IIIb, IVb, Vb, and VIb, which are all covalent. They are listed in Table 3.7.

Table 3.7
Hydrides Used in CVD (Partial List)^{[1][6]}

Element	Name	Formula	Boiling Point °C
As	Arsine	AsH ₃	-55
B	Diborane	B ₂ H ₆	-92
Ge	Germane	GeH ₄	-88
N	Ammonia	NH ₃	-33
P	Phosphine	PH ₃	-87
S	Hydrogen sulfide	H ₂ S	-60
Sb	Stibine	SbH ₃	-17
Se	Hydrogen selenide	H ₂ Se	3
Si	Silane	SiH ₄	-111
Te	Hydrogen telluride	H ₂ Te	-2

Note: Most of these compounds are extremely toxic. Manufacturer's recommendations must be carefully followed.

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4

Metallo-Organic CVD (MOCVD)

1.0 INTRODUCTION

Metallo-organic CVD (MOCVD) is a specialized area of CVD, which is a relatively newcomer, as its first reported use was in the 1960s for the deposition of indium phosphide and indium antimonide. These early experiments demonstrated that deposition of critical semiconductor materials could be obtained at lower temperature than conventional thermal CVD and that epitaxial growth could be successfully achieved. The quality and complexity of the equipment and the diversity and purity of the precursor chemicals have steadily improved since then and MOCVD is now used on a large scale, particularly in semiconductor and opto-electronic applications.^{[1][2]}

Metallo-organics are compounds in which the atom of an element is bound to one or more carbon atoms of an organic hydrocarbon group. Many of the elements used in MOCVD are the metals of groups IIa, IIb, IIIb, IVb, Vb, and VIb, which are non-transitional. The metallo-organics thus complement the halides and carbonyls, which are the precursors for the deposition of transition metals (Groups IVa, Va, and VIa) and their compounds.

The term *metallo-organic* is used somewhat loosely in CVD parlance, since it includes compounds of elements, such as silicon, phosphorus, arsenic, selenium, and tellurium, that are not considered metallic. To conform to what appears to be a well-established tradition, such nonmetal compounds will be included here as metallo-organics.

2.0 MOCVD PROCESS AND EQUIPMENT

Most MOCVD reactions occur in the temperature range of 300–800°C and at pressure varying from less than 1 Torr to atmospheric. A typical reactor for the deposition of the optoelectronic material gallium-aluminum-arsenide (GaAlAs) is shown in Fig. 4.1. Because of the highly critical requirements of most semiconductor applications, it is necessary to use the most accurate controls and high-purity reactants. Electronic mass-flow controllers, ultrafast bellows-sealed gas-switching valves, accurate venting controls, and complete elimination of dead space allow rapid switching of gases. As a result, deposits of less than 10 nm in thickness and with abrupt interfaces of less than 1 nm can be produced.^[3]

The equipment and chemicals used in MOCVD are all available commercially but are expensive and production cost is high. For these reasons, MOCVD is considered in applications where high quality is essential.

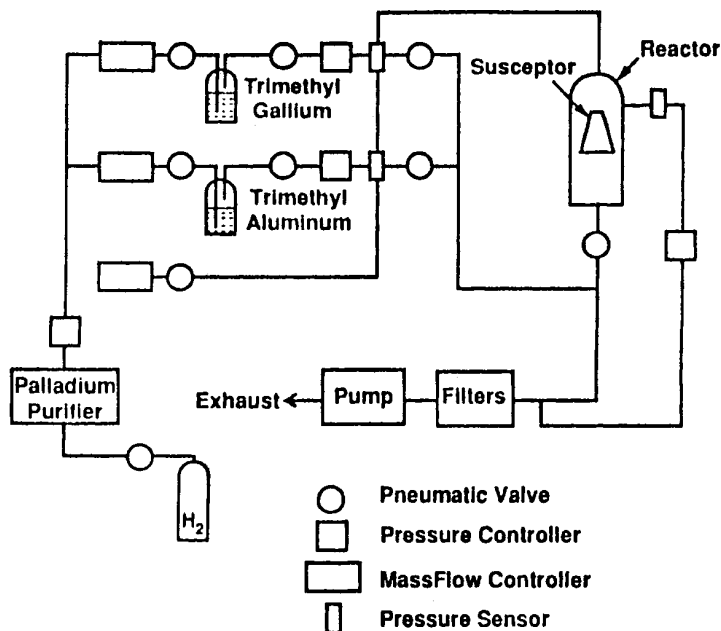


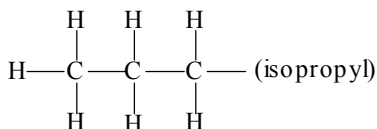
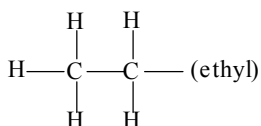
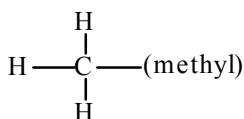
Figure 4.1. Schematic of typical MOCVD system.

3.0 MOCVD PRECURSORS: ALKYL, ALICYCLIC, AND ARYL COMPOUNDS

In the following sections, the major categories of metallo-organic compounds used in CVD are reviewed. Others are described in the review of materials produced by CVD in Chs. 6–12. These metallo-organics form only a small proportion of the total number of compounds available and there are many that could be profitably investigated.

3.1 Alkyls

A major MOCVD group is that of the alkyls. These are formed by reacting an aliphatic hydrocarbon or an alkyl halide with a metal.^[4] These hydrocarbons are composed of chains of carbon atoms as shown below:^[5]

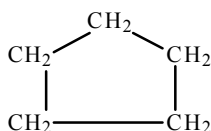


These alkyls are nonpolar volatile liquids. The methyl metallo-organics start to decompose at 200°C and the ethyl metallo-organics at approximately 110°C.

3.2 Alicyclic Compounds

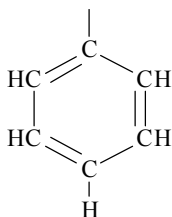
Other common MOCVD compounds are produced from alicyclic hydrocarbons, where the carbon chain forms a ring, such as in

cyclopentane shown below:



3.3 Aryl Compounds

Other MOCVD compounds are the aryls, which are formed from aromatic hydrocarbons, that is compounds that have six-member rings with three carbon double bonds, such as phenyl shown below:



Common metallo-organic alkyls, alicyclic, and aryl compounds and their relevant properties are listed in Table 4.1.^[6] Many additional organometallic compounds are available commercially as listed in Ref. 7.

Most metallo-organic compounds are monomers with some important exceptions, such as trimethyl aluminum which is a dimer. Their vapor pressures are usually directly related to the molecular weight, with the lower molecular weight compounds having the higher volatility.

To be useful as CVD precursors, a metallo-organic compound should be stable at room temperature so that its storage and transfer are not a problem. It should also decompose readily at low temperature, i.e., below 500°C. The compounds listed in Table 4.1 meet these conditions with the exception of the alkyls of arsenic and phosphorus, which decompose at higher temperatures. For that reason, the hydrides of arsenic and phosphorus are often preferred as CVD precursors (see Ch. 3). These hydrides however are extremely toxic and environmental considerations may restrict their use.

Table 4.1
Alkyls, Alicyclic, and Aryl Metallo-Organic Compounds

Compound	Formula	Type	MP°C	BP°C	Vapor Pressure mm
Trimethyl aluminum	(CH ₃) ₃ Al	Alkyl	15	126	8.4 @0°C
Triethyl aluminum	(C ₂ H ₅) ₃ Al	Alkyl	-58	194	
Triisobutyl aluminum	(C ₄ H ₉) ₃ Al	Alkyl	4	130	
Diisobutyl aluminum hydride	(C ₄ H ₉) ₂ AlH	Alkyl	-70	118	
Trimethyl arsenic	(CH ₃) ₃ As	Alkyl			238 @20°C
Diethyl arsine	(C ₂ H ₅) ₂ AsH ₂	Alkyl			0.8 @8°C
Diethyl beryllium	(C ₂ H ₅) ₂ Be	Alkyl	12	194	
Diphenyl beryllium	(C ₆ H ₅) ₂ Be	Aryl			
Dimethyl cadmium	(CH ₃) ₂ Cd	Alkyl	4	105	28 @20°C
Heptane dionato cesium	(TMHD) ₄ Ce	Alkyl	250(dec.)		0.05 @130
Trimethyl gallium	(CH ₃) ₃ Ga	Alkyl	-15	5	64 @0°C
Triethyl gallium	(C ₂ H ₅) ₃ Ga	Alkyl	-82	143	18 @48°C
Dimethyl mercury	(CH ₃) ₂ Hg	Alkyl	96		
Cyclopentadienyl mercury	(C ₅ H ₅) ₂ Hg	Cyclic			
Trimethyl indium	(CH ₃) ₃ In	Alkyl	88	134	1.7 @20°C
Triethyl indium	(C ₂ H ₅) ₃ In	Alkyl	-32	184	3 @53°C
Diethyl magnesium	(C ₂ H ₅) ₂ Mg	Alkyl			
Cyclopentadienyl magnesium	(C ₅ H ₅) ₂ Mg	Cyclic	176		
Ter-butyl phosphine	(C ₄ H ₉)PH ₂	Alkyl			285 @23°C
Triethyl phosphorus	(C ₂ H ₅) ₃ P	Alkyl			10.8 @20°C
Tetramethyl lead	(CH ₃) ₄ Pb	Alkyl			
Tetraethyl lead	(C ₂ H ₅) ₄ Pb	Alkyl			

(Cont'd)

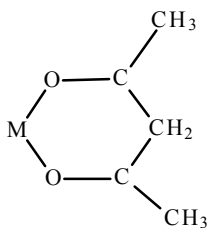
Table 4.1 (Cont'd)

Compound	Formula	Type	MP°C	BP°C	Vapor Pressure mm
Diethyl sulfur	(C ₂ H ₅) ₂ S	Alkyl			
Trimethyl antimony	(CH ₃) ₃ Sb	Alkyl			
Trimethyl tin	(CH ₃) ₃ Sn	Alkyl			
Cyclopentadienyl tin	(C ₅ H ₅) ₂ Sn	Cyclic			
Diethyl telluride	(C ₂ H ₅) ₂ Te	Alkyl			7@20°C
Terakis dimethylamine titanium	[N(CH ₃) ₂] ₄	Alkyl			
Dimethyl zinc	(CH ₃) ₂ Zn	Alkyl	-42	46	124@0°C
Diethyl zinc	(C ₂ H ₅) ₂ Z	Alkyl	-28	118	6.4@20°C

Note: Most of these compounds are extremely reactive, especially the lower alkyls. Most of them are volatile, pyrophoric and in some cases react explosively on contact with water. Some are toxic. Manufacturer's recommendations must be carefully studied before use.

4.0 ACETYLACETONATE COMPOUNDS

Metal acetylacetonates (M-ac.ac), also known as pentanedionates, are produced by reacting metals and acetylacetone. They have the following chemical structure:



The acetylacetonates are stable in air and readily soluble in organic solvents. From this standpoint, they have the advantage over the alkyls and other alkoxides, which, with the exception of the iron alkoxides, are not as easily soluble. They can be readily synthesized in the laboratory. Many are used extensively as catalysts and are readily available. They are also used in CVD in the deposition of metals such as iridium, scandium and rhenium and of compounds, such as the yttrium-barium-copper oxide complexes, used as superconductors.^{[8][9]} Commercially available acetyl-acetonates are shown in Table 4.2.

Also increasingly common, as CVD precursors, are many halogen-acetylacetonate complexes, such as trifluoro-acetylacetonate thorium, $\text{Th}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_4$, used in the deposition of thoriated tungsten for thermionic emitters,^[10] the trifluoro-acetylacetonates of hafnium and zirconium and the hexafluoro-acetylacetonates of calcium, copper, magnesium, palladium, strontium, and yttrium.

5.0 MOCVD REACTIONS FOR THE DEPOSITION OF METALS

Most metals can be deposited by MOCVD and in some cases the process is an important industrial operation. The metals most readily deposited by MOCVD are the non-transition metals. The following is a summary of the metallo-organic precursors and deposition condition presently used in development or production.

Table 4.2
Acetyl-Acetonates Organo-Metallic Compounds

Metal	Formula	Form	Melting Point °C
Barium	Ba(C ₅ H ₇ O ₂) ₂	Crystal	>320
Beryllium	Be(C ₅ H ₇ O ₂) ₂	White crystal	108
Calcium	Ca(C ₅ H ₇ O ₂) ₂	White crystal	175 dec.
Cerium	Ce(C ₅ H ₇ O ₂) ₃	Yellow crystal	131
Chromium	Cr(C ₅ H ₇ O ₂) ₃	Violet crystal	214
Cobalt	Co(C ₅ H ₇ O ₂) ₃	Green powder	240
Copper	Cu(C ₅ H ₇ O ₂) ₂	Blue crystal	230 (s)
Dysprosium	Dy(C ₅ H ₇ O ₂) ₃	Powder	
Erbium	Er(C ₅ H ₇ O ₂) ₃	Powder	
Gadolinium	Gd(C ₅ H ₇ O ₂) ₃	Powder	143
Indium	In(C ₅ H ₇ O ₂) ₃	Cream powder	186
Iridium	Ir(C ₅ H ₇ O ₂) ₃	Orange crystal	
Iron	Fe(C ₅ H ₇ O ₂) ₃	Orange powder	179
Lanthanum	La(C ₅ H ₇ O ₂) ₃	Powder	
Lead	Pb(C ₅ H ₇ O ₂) ₂	Crystal	
Lithium	LiC ₅ H ₇ O ₂	Crystal	ca 250
Lutetium	Lu(C ₅ H ₇ O ₂) ₃	Powder	
Magnesium	Mg(C ₅ H ₇ O ₂) ₂	Powder	dec.
Manganese	Mn(C ₅ H ₇ O ₂) ₂	Buff crystal	180
Neodymium	Nd(C ₅ H ₇ O ₂) ₃	Pink powder	150
Nickel	Ni(C ₅ H ₇ O ₂) ₂	Powder	238
Palladium	Pd(C ₅ H ₇ O ₂) ₂	Orange needle	210
Platinum	Pt(C ₅ H ₇ O ₂) ₂	Yellow needle	
Praseodymium	Pr(C ₅ H ₇ O ₂) ₃	Powder	
Rhodium	Rh(C ₅ H ₇ O ₂) ₃	Yellow crystal	
Samarium	Sm(C ₅ H ₇ O ₂) ₃	Powder	146
Scandium	Sc(C ₅ H ₇ O ₂) ₃	Powder	187
Silver	AgC ₅ H ₇ O ₂	Crystal	
Strontium	Sr(C ₅ H ₇ O ₂) ₂	Crystal	220
Terbium	Tb(C ₅ H ₇ O ₂) ₃	Powder	
Thorium	Th(C ₅ H ₇ O ₂) ₄	Crystal	171 (s)
Thulium	Tm(C ₅ H ₇ O ₂) ₃	Powder	
Vanadium	V(C ₅ H ₇ O ₂) ₃	Powder	
Ytterbium	Yb(C ₅ H ₇ O ₂) ₃	Powder	
Yttrium	Y(C ₅ H ₇ O ₂) ₃	Powder	
Zinc	Zn(C ₅ H ₇ O ₂) ₂	Needle	138 (s)
Zirconium	Zr(C ₅ H ₇ O ₂) ₄	White crystal	172

Note: (s) indicates that the compound sublimates at atmospheric pressure before melting.

5.1 Aluminum^{[10][11]}

Decomposition of the following alkyls at 200–300°C up to 1 atm.

- Trimethyl aluminum, $(\text{CH}_3)_3\text{Al}$ or TMA.
- Triethyl aluminum, $(\text{C}_2\text{H}_5)_3\text{Al}$ or TEA.
- Tri-isobutyl aluminum, $(\text{C}_4\text{H}_9)_3\text{Al}$ or TIBA.
- Dimethyl aluminum hydride, $(\text{CH}_3)_2\text{AlH}$ or DMAH (preferred reaction).

5.2 Cadmium^[13]

- Decomposition of dimethyl cadmium, $\text{Cd}(\text{CH}_3)_2$, at 10 Torr with argon laser.

5.3 Chromium^{[14][15]}

- Decomposition of dicumene chromium, $(\text{C}_9\text{H}_{12})_2\text{Cr}$, at 320–545°C (possible inclusion of carbon or hydrogen in the deposit).

5.4 Copper^{[16]–[18]}

- Decomposition of copper acetylacetonate, $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ at 260–340°C.
- Hydrogen reduction of copper chelate, $\text{Cu}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C.
- Decomposition of copper hexafluoroacetylacetonate at 200°C.

5.5 Gold^[19]

- Decomposition of dimethyl 1-2,4 pentadionate gold, or dimethyl-(1,1,1-trifluoro-2-4-pentadionate) gold, or dimethyl-(1,1,1-5,5,5 hexafluoro 2-4 pentadionate) gold.

5.6. Nickel^[20]

- Hydrogen reduction of nickel alkyl, $\text{Ni}(\text{C}_5\text{H}_5)_2$ at 200°C, or nickel chelate, $\text{Ni}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C.

5.7. Platinum^{[13][21]}

- Decomposition of platinum hexafluoro-2,4-pentadionate, $\text{Pt}(\text{CF}_3\text{COCHCOCF}_3)_2$, or tetrakis-trifluorophosphine, $\text{Pt}(\text{PF}_3)_4$ at 200–300°C in hydrogen.

5.8. Iridium^{[22][23]}

- Decomposition of acetyl acetate, $\text{Ir}(\text{CH}_3\text{COCHCOCH}_3)_3$ at 400–450°C and 1 atm.

5.9. Rhodium^[22]

- Decomposition of rhodium acetyl acetate, $\text{Rh}(\text{CH}_3\text{COCHCOCH}_3)_3$ at 250°C and 1 atm. Decomposition of rhodium trifluoro-acetyl acetate, $\text{Rh}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$ at 400°C and 1 atm.

5.10 Tin^[24]

- Decomposition of tetramethyl or triethyl tin, $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}_2(\text{C}_2\text{H}_5)_3$ at 500–600°C at low pressure.

5.11 Titanium^{[25][26]}

- Decomposition of tris-(2,2'-bipyridine) titanium at < 600°C (deposit tends to retain impurities such as C, N_2 , and H_2).

6.0 MOCVD REACTIONS FOR THE DEPOSITION OF CARBIDES AND NITRIDES

Many CVD reactions are being investigated for the deposition of carbides and nitrides, particularly for titanium nitride for semiconductor applications, such as diffusion barrier. The following is a summary of the metallo-organic precursors and deposition condition presently used in development or production of these materials.

6.1 Chromium Carbide^[27]

- Decomposition of chromium dicumene $\text{Cr}[(\text{C}_6\text{H}_5)\text{C}_3\text{H}_7]_2$ at 300–550°C and 0.5–50 Torr.

6.2 Titanium Carbide^[28]

- Decomposition of tris-(2,2'-bipyridine) titanium at 370–520°C.
- Decomposition of tetra-n-pentyl titanium at 150–300°C.

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- Decomposition of dichlorotitacene, $(C_5H_5)_2TiCl_2$, (substrate temperature is 700°C).

6.3 **Aluminum Nitride**^{[29]–[32]}

- Reaction of ammonia (NH_3) with trimethyl aluminum $(CH_3)_3Al$ at 900°C and < 1 Torr).
- Pyrolysis of diethyl aluminum azide $[(C_2H_5)_2AlN_3]$ at 450–870°C).
- Pyrolysis of hexakis(dimethylamido)dialuminum with ammonia at 200–250°C at 1 atm.

6.4 **Boron Nitride**^[33]

- Reaction of ammonia (NH_3) with triethyl boron $B(C_2H_5)_3$ in a H_2 and Ar at 750–1200°C.

6.5 **Silicon Nitride**^[34]

- Reaction of ammonia (NH_3) with tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$ at 200–400°C.

6.6 **Titanium Nitride**^{[35]–[38]}

- Reaction of tetrakis-diethylamino titanium (TDEAT) or tetrakis-dimethylamino titanium (TDMAT) with ammonia (NH_3) at 300°C in a flow of helium. Possible carbon retention.
- Pyrolysis of tetrakis(dimethylamido)titanium (TDMAT) in nitrogen at 300°C.

7.0 MOCVD REACTIONS FOR THE DEPOSITION OF OXIDES

7.1 Aluminum Oxide^[39]

- Pyrolysis of aluminum isopropoxide, $\text{Al}(\text{OC}_3\text{H}_7)_3$ at 900°C .
- Decomposition of aluminum alkyls, such as $(\text{CH}_3)_3\text{Al}$ or $(\text{C}_2\text{H}_5)_3\text{Al}$ in O_2 or N_2O at $250\text{--}500^\circ\text{C}$.

7.2 Chromium Oxide^[40]

- Decomposition of chromium acetyl acetonate, $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ at $520\text{--}560^\circ\text{C}$.

7.3 Hafnium Oxide^[41]

- Pyrolysis of hafnium acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_3$, at $400\text{--}750^\circ\text{C}$ or hafnium trifluoro-acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_4\text{O}_2\text{F}_3)_4$ at $500\text{--}550^\circ\text{C}$ with helium and oxygen as carrier gases.

7.4 Iron Oxide^[42]

- Decomposition of acetylacetonate, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, at $400\text{--}500^\circ\text{C}$, or of the iron trifluoro-acetylacetonate, $\text{Fe}(\text{F}_3\text{C}_5\text{H}_4)_3$, at 300°C in oxygen.
- Decomposition of iron cyclopentadienyl, $(\text{C}_5\text{H}_5)_2\text{Fe}$, in O_2 at $300\text{--}500^\circ\text{C}$ and 1–20 Torr.

7.5 Silicon Dioxide^{[43]–[47]}

- Decomposition of tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, at 700°C and <1 Torr, in the presence of ozone.
- Decomposition of diacetoxy-ditertiarybutoxy silane (DADBS) at 450–550°C and <1 Torr.
- Decomposition of octamethyl-cyclotetrasiloxane in ozone at 400°C at low pressure.

7.6 Tantalum Oxide^{[48][49]}

- Pyrolysis of tantalum ethylate, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, in O_2 and nitrogen at 340–450°C and <1 Torr.
- Pyrolysis of tantalum dichlorodiethoxyacetylacetonate at 300–500°C.

7.7 Tin Oxide^{[50]–[52]}

- Oxidation of tetramethyl tin at atmospheric pressure or <1 Torr) at 350–600°C.
- Reaction of dimethyl tin chloride, $(\text{CH}_3)_2\text{SnCl}_2$, with O_2 at 540°C.

7.8 Titanium Oxide^{[53][54]}

- Pyrolysis of titanium ethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ in O_2 and He at 450°C.
- Pyrolysis on titanium tetraisopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in O_2 at 300°C and <1 Torr.

7.9 Zinc Oxide^[55]

- Reaction of dimethyl zinc and tetrahydrofuran (THF) at 300–500°C, at low pressure.

7.10 Zirconium Oxide^{[56][57]}

- Yttria-stabilized zirconia by codeposition of tetramethyl heptadione of zirconium and yttrium, $\text{Zr}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ and $\text{Y}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ at 735°C.
- Decomposition of the trifluoro-acetylacetonates in He above 300°C.

7.11 Titanates^{[58]–[61]}

- Lead titanate (PbTiO_3) by reacting ethyl titanate and lead vapor in oxygen and nitrogen at 500–800°C.
- Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) by reacting triphenyl bismuth, $\text{Bi}(\text{C}_6\text{H}_5)_3$ and titanium isopropoxide at 600–800°C and 5 Torr.
- Strontium titanate (SrTiO_3) by reacting titanium isopropoxide and a strontium beta-diketonate complex at 600–850°C and 5 Torr.

7.12 Superconductors^{[62][83]}

- $\text{YBa}_2\text{Cu}_3\text{O}_7$ from acetylacetonates (tetramethyl heptadionate) of yttrium, barium, and copper, at 825°C and 5 Torr.

8.0 MOCVD REACTIONS FOR THE DEPOSITION OF III–V AND II–VI COMPOUNDS

Note: See Ch. 12 for more details

8.1 III–V Compounds^{[64][65]}

- Reaction of an alkyl (usually trimethyl) of Group-IIIb element (Al, Ga, In) with a hydride of a Group-Vb element (P, As, Sb) at 600–800°C and 1 atm.^{[41][42]} P-doping obtained from addition of diethyl zinc or bis(cyclopentadienyl) magnesium.

8.2 II–VI Compounds

- Reaction of a vaporized metal of Group II (Zn, Cd, Hg) and alkyl of Group VI element (Te, Se) at 325–350°C.

9.0 GENERAL APPLICATIONS OF MOCVD

Table 4.3. is a summary of the major applications of MOCVD. More details are found in Chs. 13–16.^[2]

Table 4.3.
Applications of MOCVD

GaAs/AlGaAs photocathodes, solar cells, lasers, HEMATs,
high-power LEDs, MESFETs
InP/InGaAsP long-wavelength lasers and detectors
InP/InGaAs quantum wells, solar cells, detectors
GaAs on Si wafers
GaAs/InGaP HBTs
GaAs/AlGaInP visible lasers, orange LEDs
HgCdTe detectors

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