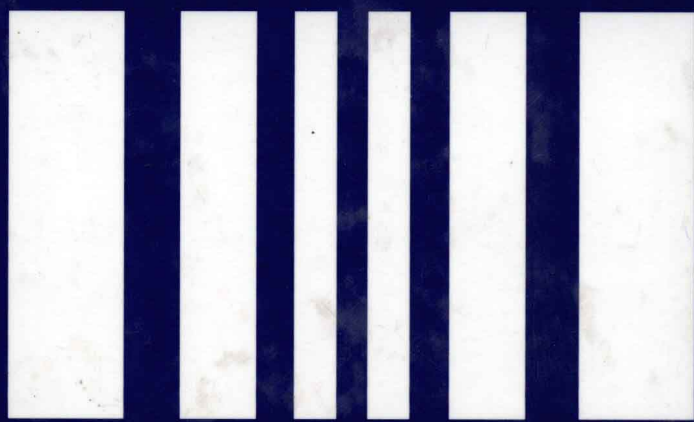


**CHEMICAL  
VAPOR  
DEPOSITED  
MATERIALS**



**FRANCIS S. GALASSO**

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## PREFACE

Chemical vapor deposition (CVD) has grown in importance as a means of producing solid materials from gaseous reactants. It is particularly useful in the preparation of complex shapes and in the deposition of coatings in difficult to reach sites.

CVD has been widely used in the processing of semiconductors, but interest has grown in recent years in the formation of high temperature ceramic materials, grown to a point where most material laboratories wish to acquire this technology. Materials such as SiC, Si<sub>3</sub>N<sub>4</sub>, and BN and other carbides, nitrides, and borides are needed to improve tool bits, to improve the wear resistance of materials and to provide oxidation resistance or diffusion barriers in composite structures. Producing coatings for fibers has become an important area of development and will continue to grow in importance.

This book was written to provide a knowledge of how to prepare these high temperature materials and to present their structures and properties so that interested scientists can use this information in their work. The first chapter provides basic information on CVD, the second covers CVD Si<sub>3</sub>N<sub>4</sub>, the third presents information on CVD SiC and the fourth chapter covers CVD BN. The materials were selected because of the growing interest in these particular phases. The fifth chapter covers other carbides, borides, and nitrides, which are also important in ceramic technology. Some metals are also included because they are often reacted with deposition surfaces to produce ceramic phases.

This book is not intended as a review of CVD in semiconductor technology, which is well covered elsewhere, nor is it intended as a complete review of CVD materials. Instead, it is written as a concise presentation of some of the most important materials required in the development of high temperature technology.

I wish to thank Sue Cebula for assistance in the preparation of this book and Dan Moroz for X-ray data.

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# 1 Introduction

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The recent wave of interest in Chemical Vapor Deposition (CVD) as a means of producing solid materials from gases may be the largest since the days of de Lodyguine<sup>1</sup> and van Arkel et al.<sup>2</sup> The value of CVD in electronics has been known because it provides a means of placing pure and doped materials at specific locations on microcircuits. In general, the low temperature processes are selected for these applications so that the substrate will not be damaged. This means that CVD processes for electronics often involve the most reactive species, for example, hydrides rather than halides. While care has to be taken in handling CVD reactants in general, this is particularly important in semiconductor research where the gases are often phosphoric or toxic.

As semiconductor technology has developed the CVD equipment employed has become more sophisticated and sensors have been used to make the handling of these CVD gases much safer. In many cases, plasma-assisted CVD has been used to reduce the temperature of deposition even further or so that less reactive gases could be used. The electronic CVD technology has continued to improve with automation; gas control and reactor technology developed to a point where optical and electronic devices are routinely fabricated. This is not true of high temperature CVD technology where producing solids from gaseous species at high temperatures presents difficult and unique problems. Some of these materials and conditions for preparing them are listed in Table 1.1. High temperature solid materials are desired which do not contain entrapped gases and have high densities which often cannot be achieved in low temper-

**Table 1.1**  
**CERAMIC MATERIALS PRODUCED BY CHEMICAL**  
**VAPOR DEPOSITION**

Coatings	Chemical Mixture	Deposition Temp. (°C)	Method	Application
<b>Carbides</b>				
TiC	TiCl <sub>4</sub> -CH <sub>4</sub> -H <sub>2</sub>	900-1000	CCVD	wear
	TiCl <sub>4</sub> -CH <sub>4</sub> (C <sub>2</sub> H <sub>2</sub> )-H <sub>2</sub>	400-600	PACVD	elec
HfC	HfCl <sub>x</sub> -CH <sub>4</sub> -H <sub>2</sub>	900-1000	CCVD	wear, cor/ox
ZrC	ZrCl <sub>4</sub> -CH <sub>4</sub> -H <sub>2</sub>	900-1000	CCVD	wear, cor/ox
	ZrBr <sub>4</sub> -CH <sub>4</sub> -H <sub>2</sub>	>900	CCVD	wear, cor/ox
SiC	CH <sub>3</sub> SiCl <sub>3</sub> -H <sub>2</sub>	1000-1400	CCVD	wear, cor/ox
	SiH <sub>4</sub> -C <sub>x</sub> H <sub>y</sub>	200-500	PACVD	elec, cor
B <sub>4</sub> C	BCl <sub>3</sub> -CH <sub>4</sub> -H <sub>2</sub>	1200-1400	CCVD	wear
B <sub>x</sub> C	B <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub>	400	PACVD	wear, elec, cor
W <sub>2</sub> C	WF <sub>6</sub> -CH <sub>4</sub> -H <sub>2</sub>	400-700	CCVD	wear
Cr <sub>7</sub> C <sub>3</sub>	CrCl <sub>2</sub> -CH <sub>4</sub> -H <sub>2</sub>	1000-1200	CCVD	wear
Cr <sub>3</sub> C <sub>2</sub>	Cr(CO) <sub>6</sub> -CH <sub>4</sub> -H <sub>2</sub>	1000-1200	CCVD	wear
TaC	TaCl <sub>5</sub> -CH <sub>4</sub> -H <sub>2</sub>	1000-1200	CCVD	wear, elec
VC	VCl <sub>2</sub> -CH <sub>4</sub> -H <sub>2</sub>	1000-1200	CCVD	wear
NbC	NbCl <sub>5</sub> -CCl <sub>4</sub> -H <sub>2</sub>	1500-1900	CCVD	wear
<b>Nitrides</b>				
TiN	TiCl <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	900-1000	CCVD	wear
	TiCl <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	250-1000	PACVD	elec
HfN	HfCl <sub>x</sub> -N <sub>2</sub> -H <sub>2</sub>	900-1000	CCVD	wear, cor/ox
	HfI <sub>4</sub> -NH <sub>3</sub> -H <sub>2</sub>	>800	CCVD	wear, cor/ox
Si <sub>3</sub> N <sub>4</sub>	SiCl <sub>4</sub> -NH <sub>3</sub> -H <sub>2</sub>	1000-1400	CCVD	wear, cor/ox
	SiH <sub>4</sub> -NH <sub>3</sub> -H <sub>2</sub>	250-500	PACVD	elec, cor/ox
	SiH <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	300-400	PACVD	elec
BN	BCl <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	1000-1400	CCVD	wear
	BCl <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	25-1000	PACVD	elec
	BH <sub>3</sub> -N(C <sub>2</sub> H <sub>5</sub> )-Ar	25-1000	PACVD	elec
	B <sub>3</sub> N <sub>3</sub> H <sub>6</sub> -Ar	400-700	CCVD	elec, wear
	BF <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	1000-1300	CCVD	wear
ZrN	B <sub>2</sub> H <sub>6</sub> -NH <sub>3</sub> -H <sub>2</sub>	400-700	PACVD	elec
	ZrCl <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	1100-1200	CCVD	wear, cor/ox
TaN	ZrBr <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	>800	CCVD	wear, cor/ox
	TaCl <sub>5</sub> -N <sub>2</sub> -H <sub>2</sub>	800-1500	CCVD	wear
AlN	AlCl <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	800-1200	CCVD	wear

**Table 1.1 (continued)**  
**CERAMIC MATERIALS PRODUCED BY CHEMICAL**  
**VAPOR DEPOSITION**

Coatings	Chemical Mixture	Deposition Temp. (°C)	Method	Application
VN	AlBr <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	800-1200	CCVD	wear
	AlBr <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	200-800	PACVD	elec, wear
	Al(CH <sub>3</sub> ) <sub>3</sub> -NH <sub>3</sub> -H <sub>2</sub>	900-1000	CCVD	elec, wear
	VCl <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	900-1200	CCVD	wear
NbN	NbCl <sub>5</sub> -N <sub>2</sub> -H <sub>2</sub>	900-1300	CCVD	wear, elec
<b>Oxides</b>				
Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub>	900-1100	CCVD	wear, cor/ox
	Al(CH <sub>3</sub> ) <sub>3</sub> -O <sub>2</sub>	300-500	CCVD	elec, cor
	Al{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>3</sub> -O <sub>2</sub>	300-500	CCVD	elec, cor
	Al(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> -O <sub>2</sub>	300-500	CCVD	elec, cor
SiO <sub>2</sub>	SiH <sub>4</sub> -CO <sub>2</sub> -H <sub>2</sub>	200-600	PACVD	elec, cor
	SiH <sub>4</sub> -N <sub>2</sub> O	200-600	PACVD	elec
TiO <sub>2</sub>	TiCl <sub>4</sub> -H <sub>2</sub> O	800-1000	CCVD	wear, elec
	TiCl <sub>4</sub> -O <sub>2</sub>	25-700	PACVD	elec
	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> -O <sub>2</sub>	25-700	PACVD	elec
ZrO <sub>2</sub>	ZrCl <sub>4</sub> -CO <sub>2</sub> -H <sub>2</sub>	900-1200	CCVD	wear, cor/ox
Ta <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub> -O <sub>2</sub> -H <sub>2</sub>	600-1200	CCVD	wear, cor, elec
Cr <sub>2</sub> O <sub>3</sub>	Cr(CO) <sub>6</sub> -O <sub>2</sub>	400-600	CCVD	wear
<b>Borides</b>				
TiB <sub>2</sub>	TiCl <sub>4</sub> -BCl <sub>3</sub> -H <sub>2</sub>	800-1000	CCVD	wear, cor, elec
MoB	MoCl <sub>5</sub> -BBr <sub>3</sub>	1400-1600	CCVD	wear, cor
WB	WCl <sub>6</sub> -BBr <sub>3</sub> -H <sub>2</sub>	1400-1600	CCVD	wear, cor
NbB <sub>2</sub>	NbCl <sub>5</sub> -BCl <sub>3</sub> -H <sub>2</sub>	900-1200	CCVD	wear, cor
TaB <sub>2</sub>	TaBr <sub>5</sub> -BBr <sub>3</sub>	1200-1600	CCVD	wear, cor
ZrB <sub>2</sub>	ZrCl <sub>4</sub> -BCl <sub>3</sub> -H <sub>2</sub>	1000-1500	CCVD	wear, cor, elec
HfB <sub>2</sub>	HfCl <sub>x</sub> -BCl <sub>3</sub> -H <sub>2</sub>	1000-1600	CCVD	wear, cor

<sup>a</sup> CCVD = conventional CVD; PACVD = plasma-assisted CVD.

<sup>b</sup> Wear = wear-resistant coatings; elec = electronics; cor = corrosion-resistant coatings; ox = oxidation-resistant coatings.

After Stinton et al., *Cer. Bull.*, 67, 350 (1988).



ature deposits. It is this area of materials research and development that is growing most rapidly in interest, probably because of the desire for high density hard coatings for tool bits, coatings for fibers, coatings for ceramics and metals and lubricating coatings; many laboratories want the technology but unfortunately only a few universities are turning out CVD personnel. Because of the demand for trained CVD scientists, this situation will probably change in the future. In the meantime, it might be helpful to review what is known about the preparation of CVD materials to assist scientists who are interested in using this technology and to examine what remains to be learned.

## EQUIPMENT

Scientists, in general, know how to produce CVD materials but the details of specific preparations are often not available. The equipment involves either a hot walled (Figure 1.1) or cold walled reactor or a fluidized bed (modified hot wall reactor). In a hot walled reactor, a heater surrounds the reaction area. The heater can be heated by electrical resistance or an induction unit can be used to heat a susceptor which surrounds the substrate to be coated. The deposition is not efficient since the hot walls are coated as well as the substrate.

Variations of these reactors are also used for special purposes. For coating fibers, for example, reactive gases are passed over a conducting fiber which can be resistively heated by using mercury seal contacts at each end of a vertical silica tube.<sup>3,4</sup> Fibers such as B and SiC fibers are formed in this way using W or C fiber substrates. The fibers can also be heated using RF heating with argon seals at the ends of the reactor. In depositions which require low pressures, the spool of wire substrate and the uptake spool are all encased in a vacuum chamber with the reactor tube which is surrounded by a heater.

Chemical Vapor Infiltration (CVI) equipment is also especially designed, in this case, for obtaining good penetration of the CVD matrix into a bundle of fibers. If the fiber preform is heated externally, the composite will seal off and the surface has to be continuously ground and reimpregnated to get good matrix penetration. In one reactor configuration, a carbon man-

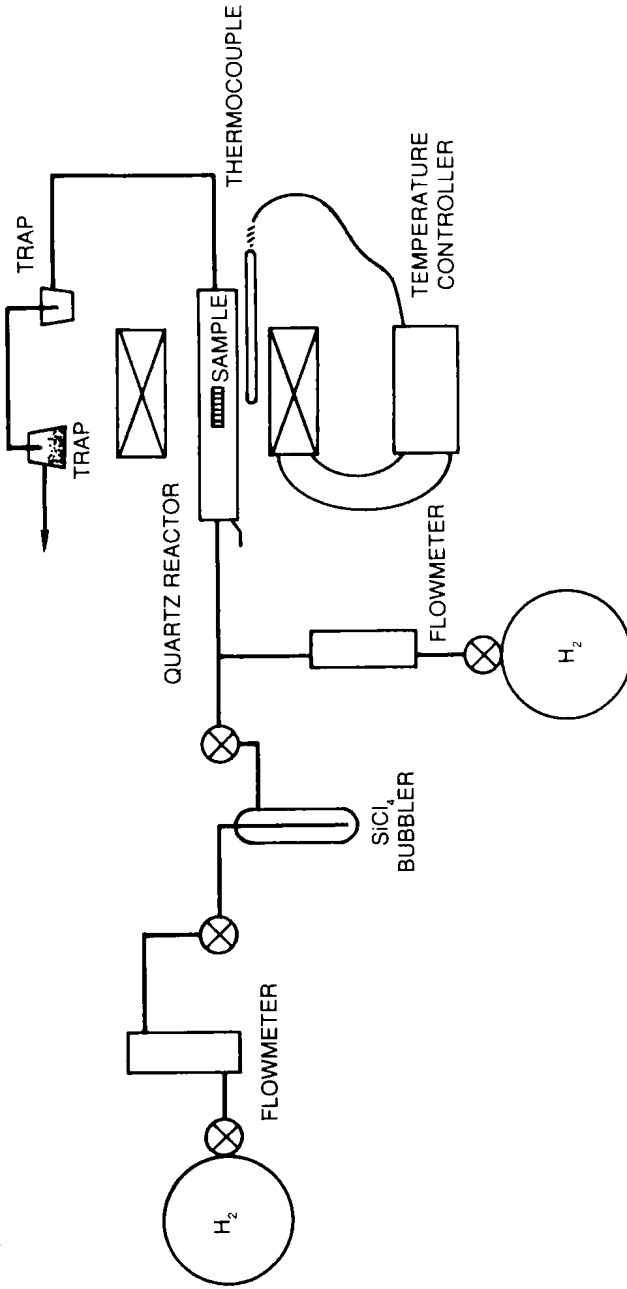


FIGURE 1.1. CVD Reactor. (After Hwan et al., *Adv. Ceram. Mater.*, 3, 584 (1988).)

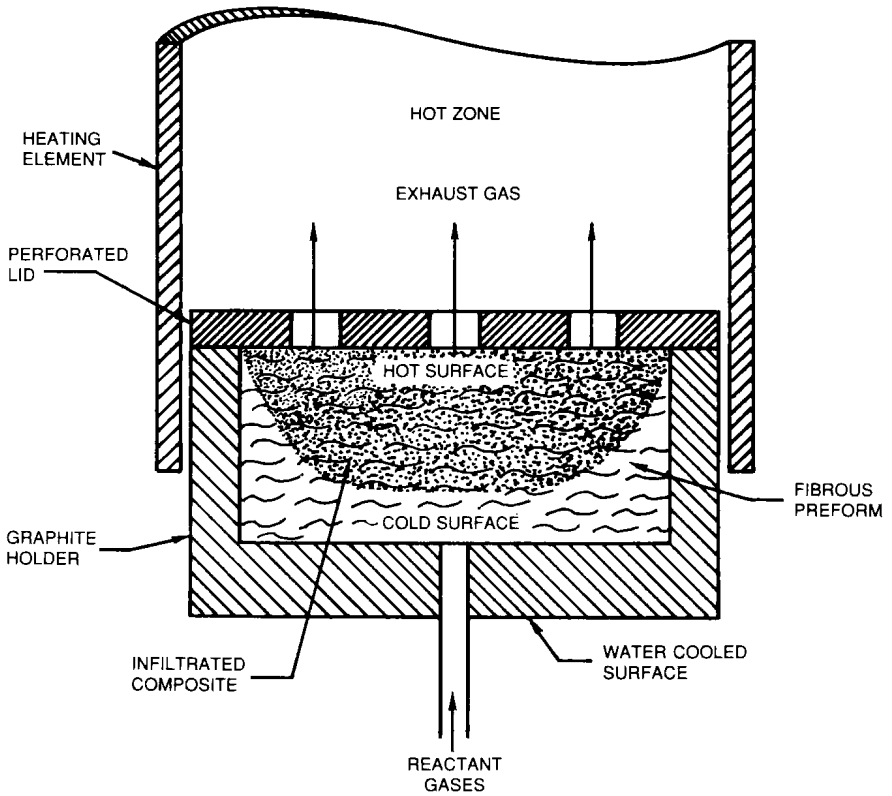


FIGURE 1.2. Schematic of process utilizing thermal and pressure gradients. (After Stinton et al., *Ceram. Bull.*, 67, 353 (1988).)

drel is heated inductively and the  $\text{SiO}_2$  reactor wall is water cooled to obtain deposition from the inside of the composite to the outside, minimizing surface seal off.<sup>5</sup> In an ORNL reactor (Figure 1.2) both a pressure and temperature gradient are produced across the fiber preform to obtain good penetration of the CVD matrix.<sup>6</sup>

The reactant gases in a CVD process are introduced separately or premixed and passed into the reaction area. This will depend on whether the gases will react before they reach the substrate which is to be avoided unless powder formation is desired.<sup>7-9</sup> In some cases, one gas is introduced through an inner tube and the other through the outer tube. If a reactant is a liquid, a carrier gas can be passed through the liquid and

then into the reaction chamber, while, if it is a solid, the carrier gas is passed over or around it (sometimes heated) before leading the vapor into the hot substrate. By controlling the temperature of the vapor, the amount of reactant introduced can be controlled. In some cases, it is useful to employ a controlled temperature condenser to make sure that the carrier gas is saturated with the reactant.

Many reactant gases can be formed by passing a gas through a heated metal. For example, chlorine can be passed through hot metals to form chlorides which are then passed into the reaction chamber. Sometimes a vapor is generated by heating a substrate resistively in a reactant liquid, leading to very rapid deposition.

The largest problem with designing the various reactors together with inlets and exhaust is that the processes are still not well understood. This is a particular problem when a process is to be scaled-up for production. It is important to know what species are present in the heated reactor, what is the concentration gradient, and what conditions result in optimum deposition (rate and properties). Studies involving reactor shapes, temperatures, gas flow rates, and number and placement of gas inlets should result in better reactor designs and parameter control. In addition, these studies should lead to the use of sensors which can be employed in controls for better automation of the process. The electronic materials CVD reactors are somewhat more advanced in this area of automation.

## GROWTH PROCESS

In most CVD processes the CVD material is formed on the surface of a substrate, but in some cases, the substrate can react with a deposit to form a compound. In cases where powder is desired, high reactant concentrations and temperatures are used deliberately so that homogeneous nucleation will take place in the gas phase.

Nucleation takes place at selected sites on the substrate surface. Then additional growth occurs by atoms adding to these surface sites and also from surface diffusion over the empty surface. The atoms can arrange themselves in some relationship to the substrate atoms to form a single crystal or a

polycrystalline body with some preferred orientation. In the absence of epitaxy, random growth takes place with some grains growing more rapidly than others and preferred orientation can occur, resulting in columnar grain. If atoms are added from the gas, predominantly small voids can exist while surface diffusion helps to produce dense material. The growth can proceed rapidly where peaks occur on the surface because of the higher concentration of reactants there in comparison to the concentration in the valleys where reactants can be more depleted. While these columnar grains are desirable for some applications, because they resist grain growth, equiaxed grains can be produced by continuous nucleation due to cold working or by the use of additives.

At high temperatures and pressures, powders are formed and, as the temperature is lowered, coarse grain deposition takes place; then finer structures and finally amorphous material are produced. Low pressures and high temperatures tend to favor epitaxial and single crystal growth.

## CHEMICAL EQUILIBRIUM

An analysis of the reaction equilibrium can be helpful in understanding a CVD process. First, a list of all of the compounds which contain the elements involved is made. To obtain the equilibrium partial pressure of each of the possible compounds, the chemical equilibria relating each of these compounds to its elemental constituents are solved simultaneously at a selected pressure and temperature. An example for SiC deposition is shown in Figure 1.3.

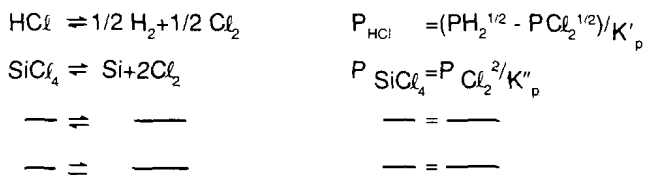
Doherty<sup>10</sup> shows how this is done using thermodynamic data from JANAF tables<sup>11</sup> and presents the results in Figure 1.4. The SiC can be produced from SiCl<sub>4</sub> and methane or from methyltrichlorosilane. He obtains the equilibrium concentration of Si and C in the gas by adding up the C and Si in the possible compounds. When the C and Si introduced in the reaction chamber are greater than the calculated equilibrium amount in the gas solution, deposition will occur. The deposition efficiency is the ratio of the excess to the amount introduced.

Examining Figure 1.4, it can be seen that the main species at about 700°C are CH<sub>4</sub> and SiCl<sub>4</sub>, but they decompose rapidly

## a) TYPICAL MOLECULAR SPECIES IN A Si-Cl-H-C GAS SYSTEM

HCl	C <sub>2</sub> H <sub>2</sub>	SiCl <sub>2</sub> H <sub>2</sub>
SiCl <sub>4</sub>	Cl	SiCl <sub>3</sub> H
CH <sub>4</sub>	CCl <sub>4</sub>	SiH <sub>4</sub>
SiCl <sub>4</sub>	H <sub>2</sub>	Si(CH <sub>3</sub> )Cl <sub>3</sub>

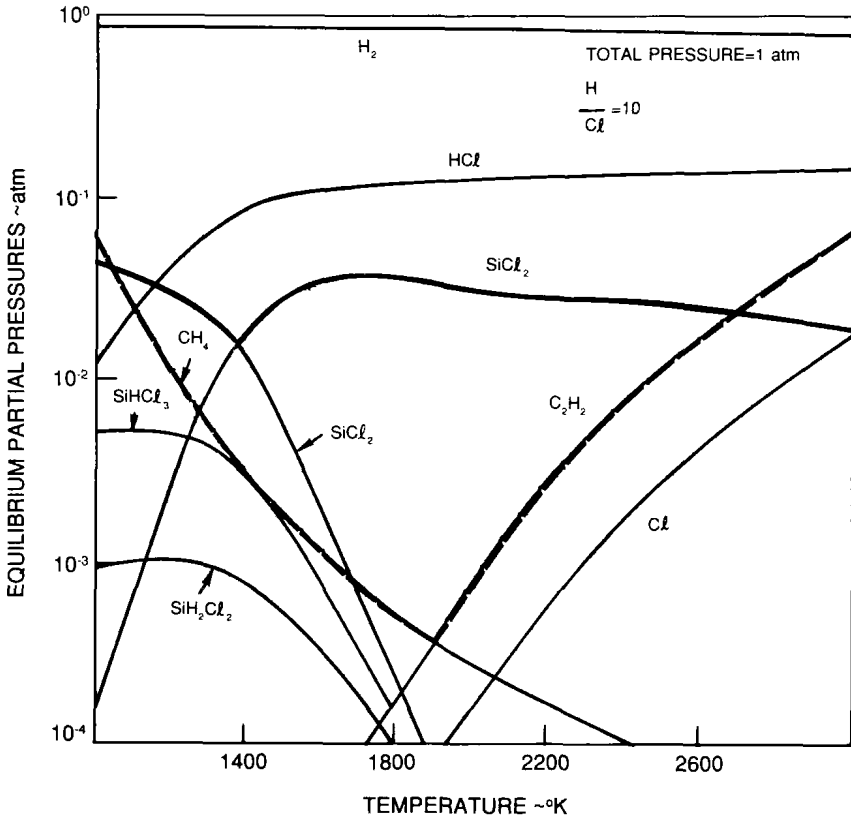
## b) CHEMICAL EQUILIBRIA



**FIGURE 1.3.** Outline of chemical equilibrium analysis for CVD of SiC from a Si, Cl<sub>2</sub>, H<sub>2</sub> and C gas system. a) lists some of the major gaseous compounds anticipated and b) is the beginning of a list of the chemical equilibrium for these compounds. The partial pressure of each compound (P<sub>x</sub>) is found by simultaneous solution of the expressions relating P<sub>x</sub> to the partial pressures of the elemental constituents, H<sub>2</sub> and Cl<sub>2</sub>. The equilibrium constants K'<sub>p</sub>, etc. can be found from listed thermodynamic data. (After Doherty, J. E., *J. Met.*, 6 (1976). Reprinted with permission from *JOM* (formerly *Journal of Metals*), a publication of The Minerals, Metals and Materials Society, Warrendale, PA.)

and the hydrogen and chlorine combine to produce HCl. At high temperatures, C<sub>2</sub>H<sub>2</sub> and SiCl<sub>2</sub> are the predominant gases. No species contains both Si and C, probably because the Si-C bond is very weak indicating that the silicon carbide is formed on the substrate by the combination of silicon and carbon.

Computer programs such as SOLGASMIX-PV<sup>12</sup> based on free-energy minimization can be used to calculate phase diagrams. Figure 1.5 shows one of these phase diagrams relating the solid deposit composition as a function of the hydrogen/silane ratio. As can be seen, high ratios can suppress carbon deposition resulting in silicon deposition with the SiC and low ratios promote C deposition with the SiC. This is probably because the effect of H<sub>2</sub> on the SiCl<sub>4</sub> + 2H<sub>2</sub> ⇌ Si + 4HCl reaction with a small equilibrium constant is greater than H<sub>2</sub> on the CH<sub>4</sub> ⇌ C + 2H<sub>2</sub> reaction with a large equilibrium constant.



**FIGURE 1.4.** Calculated equilibrium partial pressures vs. temperature for a  $H_2$ ,  $Cl_2$ , Si, C gas system with  $(H/Cl) = 10$ . The partial pressure for the dominant Si and C containing species at each temperature has been darkened for emphasis. Note that there are no important compounds in the gas system which contain both Si and C. (After Doherty, J. E., *J. Met.*, 6 (1976). Reprinted with permission from *JOM* (formerly *Journal of Metals*), a publication of The Minerals, Metals and Materials Society, Warrendale, PA.)

Satisfactory thermodynamics, however, does not insure successful deposition; a kinetically favorable process is also needed. The rate of deposition can be controlled by a reaction at or near the surface or by mass transport in the gas. This deposition on the surface can involve adsorption on the surface, a chemical reaction and desorption of the product gases. Mass transport involves moving the gas to the surface and removing the products away. If one of these mechanisms predominates, it is considered the rate controlling step, but all of these steps are involved in the deposition process.

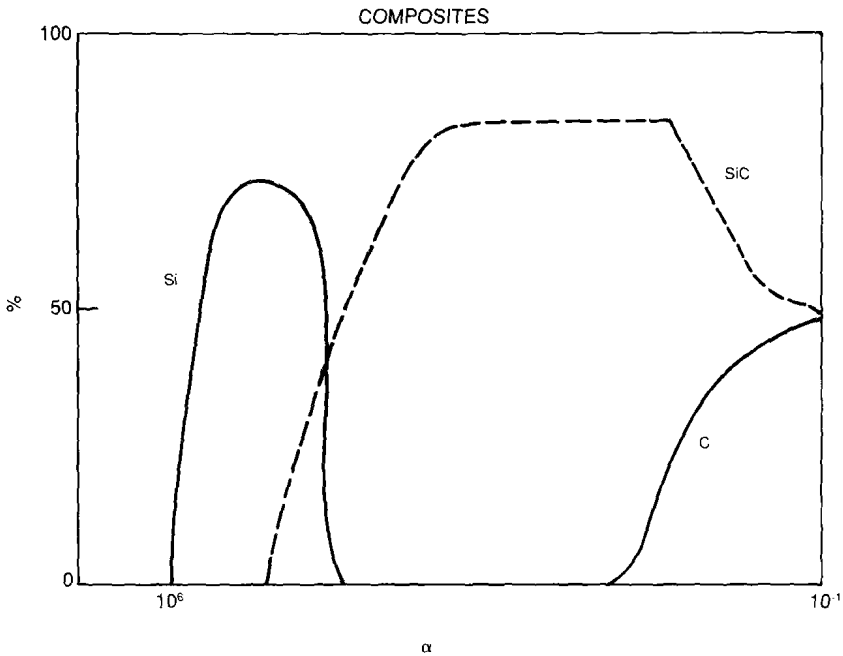


FIGURE 1.5. Percent methyltrichlorosilane reacted to form material containing Si and/or C.

To obtain the highest rates of deposition, conditions should be selected to insure mass transport control. By varying the flow rate at high flow rates, a dependence of deposition on flow rates when all other parameters are constant indicates mass transport control, and independence of deposition rate on pressure with other parameters constant is also an indication.

The resistance to mass transfer is within the layer next to the substrate surface. At low flow rates there is also an important contribution of convection to mass transport especially with gases with different specific gravities. The layer through which the gases diffuse can be as large as the reactor for low flow rates but at high flow rates the thickness of the laminar flow layer with turbulent flow around it is approximately inversely proportional to the flow velocity when the Reynolds number is more than 2100. The Reynolds number is the flow velocity times the gas density divided by the gas viscosity times the reactor diameter. Because the gas has to diffuse through this



boundary layer, the deposition rate can be increased by increasing the Reynolds number since the deposition rate is nearly proportional to the Reynolds number squared. It is important to keep the thickness of the laminar flow uniform over the part to be coated to obtain even coatings if the deposition is mass flow controlled.

The rate of deposition may also be controlled by the surface reaction. These rates can sometimes be changed by adding elements which can change the catalytic behavior of the substrate. At lower deposition rates, it is sometimes desirable to have surface kinetics control to obtain an even coating. Care must be taken, however, over large surface areas where gas depletion can change the control mechanism to mass transport control.

## COATING THICKNESS

In a reaction chamber, the deposition thickness can vary if the thermal profile is not uniform. If the thermal profile is uniform then the deposition thickness can still vary because of reactant gas depletion when the surface of the substrate is large relative to the size of the reaction chamber (see Figure 1.6). The depletion effect is shown in Figure 1.7 for W deposition. The kinetics of deposition is affected by this reaction depletion if the deposition process is mass transport controlled. Specimens are often turned to overcome this problem and other methods of alleviating this problem involve stirring the gas, using a temperature gradient and introducing fresh gas at various positions along the substrate.

An ideal method of controlling the thickness involves moving the substrate. This has been well established in fiber formation, where the fiber is drawn through mercury seals. In this case, the fiber diameter is controlled by controlling the gas composition and flow and temperature of the substrate wire. This becomes more difficult in a batch process, but means of spinning the substrate during deposition have been developed. However, in very high temperature processes, it is often more convenient to rotate or turn samples at various stages of deposition. If the furnace has to be cooled, this can be a long process, and sometimes reversing gas flow can be employed instead. The design of a reactor to obtain a uniform deposition is a critical part of the CVD process.