

# CHEMICAL VAPOR DEPOSITION

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Chemical vapor deposition :  
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*Review of Metal Deposition*  
*Tin Oxide Thin Films*  
*Novel Aluminum Precursors*  
*Single Source GaAsP Precursors*

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# Chemical Vapor Deposition

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**Essay: The first issue of CVD has arrived!** The co-editor of the new section of *Advanced Materials*, Michael Hitchman of the University of Strathclyde, sets the scene with a description of the structure, organization, and aims of CVD, a historical account of the development of chemical vapor deposition technology, and his aims in providing a useful service for the materials science, chemistry, physics, and engineering communities.

# CVD

M. L. Hitchman\*

*Chem. Vap. Deposition* 1995, 1, 5...7

A Professional Forum for the Field of Chemical Vapor Deposition

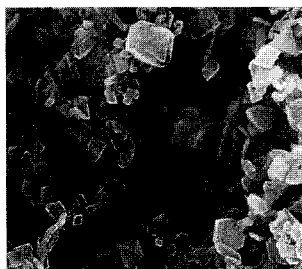
**Review: The chemical vapor deposition of metals** is a rapidly developing area in which metal-containing compounds are being synthesized as new precursors. Precursor design, reaction pathways, reactor types and the influence of the reactor operating conditions on film growth are reviewed in the first part of a two-part article. The second installment will appear in the September issue of *Advanced Materials CVD*.

M. J. Hampden-Smith,\* T. T. Kodas\*

*Chem. Vap. Deposition* 1995, 1, 8...23

Chemical Vapor Deposition of Metals:  
Part 1. An Overview of CVD Processes

**Communication: Thin films of aluminum** have an important application in the metallization of silicon devices in very large scale integration technology. In this communication a new precursor,  $\text{NMe}_2\text{AlH}(\text{Nme}_2\text{Et})$ , has been used for the CVD of high purity aluminum in the temperature range 250–350 °C. In contrast to currently available precursors it is a free flowing and non-pyrophoric liquid, making it less hazardous and more convenient for use in CVD.



A. C. Jones,\* D. J. Houlton,  
S. A. Rushworth, J. A. Flanagan,  
J. R. Brown, G. W. Critchlow

*Chem. Vap. Deposition* 1995, 1, 24...26

The Deposition of Aluminum Thin Films  
by CVD Using a Novel Adduct of  
Dimethylaluminum Hydride

**Communication: The metal oxide semiconductor  $\text{SnO}_2$**  has a range of important applications, such as in transparent and conducting coatings on glass, and in gas-sensing devices. CVD has a number of advantages as the technique of choice for the deposition of  $\text{SnO}_2$  thin films but development has in the past been hampered by the high toxicity of the available precursors and the necessity of adding an oxidant such as  $\text{O}_2$  or  $\text{H}_2\text{O}$ . Here,  $\text{SnO}_2$  deposition from the relatively non-toxic tetra-*t*-butoxide tin in the absence of added oxidant is reported. Platinum doping of the material is also discussed.

D. J. Houlton, A. C. Jones,\*  
P. W. Haycock, E. W. Williams, J. Bull,  
G. W. Critchlow

*Chem. Vap. Deposition* 1995, 1, 26...28

The Deposition of Platinum-Containing  
Tin Oxide Thin Films by Metal-Organic  
CVD

**Communication: Stoichiometrically controlled, reproducible ternary 13–15 semiconductor materials** such as GaAsP can now be produced from a single source precursor. Although these materials can be formulated using conventional multi-precursor CVD techniques, control over the stoichiometry, and thus the behavior of the semiconductors, is difficult. The synthesis and performance of the new single-source precursor are presented.

S. R. Aubuchon, M. S. Lube,  
R. L. Wells\*

*Chem. Vap. Deposition* **1995**, *1*, **28**... 31

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# Chemical Vapor Deposition of Metals: Part 1. An Overview of CVD Processes\*\*

By Mark J. Hampden-Smith\* and Toivo T. Kodas\*

The chemical vapor deposition (CVD) of metals is a rapidly developing area in which metal-containing compounds are being synthesized as new precursors. This article reviews this area and discusses precursor design, reaction pathways, reactor types, and the influence of reactor operating conditions on film growth. We have gathered recent results for precursor design and CVD chemistry and show how analysis of results from CVD experiments can be used to assist in the development of new CVD precursors.

## 1. Introduction

The chemical vapor deposition (CVD) of metal films is of scientific and technological interest due to a variety of realized and potential applications, including interconnects in microelectronic devices,<sup>[1, 2]</sup> optical tailoring of glass surfaces,<sup>[3]</sup> and membrane reactors for gas separations.<sup>[4–6]</sup> Chemical vapor deposition has a number of key advantages in depositing metal films compared to other thin film deposition techniques such as physical vapor deposition. These advantages include conformal coverage (the ability to coat a surface with complex topography with a layer of uniform thickness), selective deposition (the ability to deposit a coating on one surface, often referred to as the growth surface, and not on another, the non-growth surface), and low deposition temperatures (which can be a primary concern for thermally sensitive substrates).<sup>[7, 8]</sup> However, CVD of metals has only been adopted into industrial processes in a relatively small number of specific applications, mainly because the film properties are often not adequate or the deposition process cannot be predictably controlled to achieve a reproducible and reliable process. An example of inadequate film properties is aluminum CVD, which has been studied extensively but by which it has so far proved impossible to deposit smooth films alloyed with copper of sufficient quality for

industrial applications.<sup>[9]</sup> This phenomenon has prevented CVD of Al from being used in microelectronic applications. An example of poor reliability/predictability is selective W CVD which has not been widely adopted by the microelectronics industry because of difficulties in reproducing deposit characteristics.<sup>[10]</sup>

The CVD of an elemental material, such as a metal, is likely to be the simplest system in which to develop a detailed understanding of fundamental CVD processes, while still retaining technological relevance. As a result, there has been substantial scientific interest in CVD of metals over the past ten years and for some metals a good understanding of CVD processes exists, particularly for W, Al and Cu. However, a great deal of research is still necessary to understand specific aspects of the CVD of metals, ranging from the design requirements and thermal chemistry of metal-containing compounds to the surface reaction kinetics and mechanisms, which are both physical and chemical in nature. In addition, CVD reactor design and operation is an active area of research in which advances are required to allow reliable deposition of films.

Here, we present a review of the CVD of metals in two papers which summarize some of the information available in the book *The Chemistry of Metal CVD*.<sup>[11]</sup> This book describes the CVD of a variety of metals in detail, focusing on Al, W, Cu from Cu<sup>I</sup> and Cu<sup>II</sup> compounds, Ag, Au, Ni, Pd, Pt, and reviews the literature available for the CVD of many other metals, including those of Groups 4–9 of the periodic table. In these two review papers we provide an overview of CVD processes in general rather than discuss detailed aspects of the CVD of individual metals. The goal of these papers is to provide a general framework for classification and discussion of CVD processes. This first paper provides an overview of the basic principles of precursor design for CVD of metals, a classification of the precursors that have been used for CVD and a discussion of the attributes of different reactor types, such as hot- and cold-wall reactors and their mode of operation. In part 2,<sup>[12]</sup> the selective CVD of metals is described according to the chemical and physical origin of the selective deposition rather than for individual metals. This article addresses the surface reaction chemistry

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involved in chemical vapor deposition on substrate surfaces. A separate article deals with CVD precursor delivery and particle formation during CVD.<sup>[7]</sup>

## 2. Fundamental Aspects of CVD of Metals

Chemical vapor deposition is a method of depositing films of various materials which involves the thermally induced reaction of a metal-containing molecule on a heated surface. A schematic representation of the generalized key steps involved in a CVD process is presented in Figure 1.<sup>[2]</sup> A

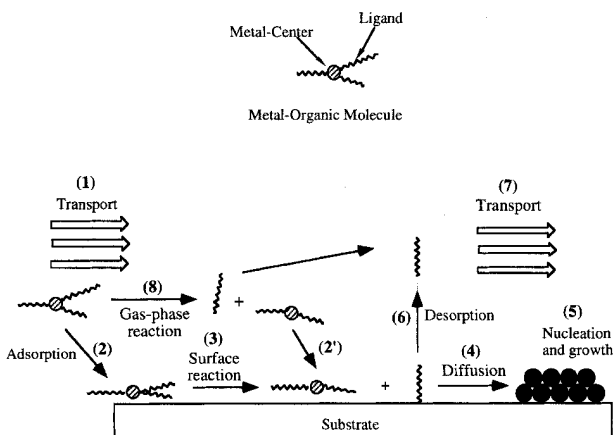


Fig. 1. Key steps involved in chemical vapor deposition.

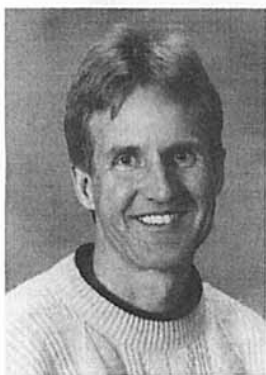
volatile precursor is transported (1) into the reactor and to the substrate, where it adsorbs (2) and reacts (3) to liberate the supporting ligands, which are subsequently desorbed (6) and transported out of the reactor (7). The metal atoms then diffuse (4) to form a stable nucleus, where subsequent growth occurs (5). Under certain circumstances gas-phase reactions (8) can also occur. The details of the surface reactions are likely to be peculiar to a particular metal-containing precursor, surface, temperature and other deposition conditions (i.e., presence of a reactive gas). Any of these steps (and some others) may be rate-limiting. Once a continuous film is formed, growth takes place on the metal being deposited. Step 1 is discussed in more detail in Section 5.

## 3. Precursor Design and Classification for CVD of Metals

The first step in CVD of any material is to consider which metal-containing molecules may be useful as precursors. The factors that affect the choice of a particular source molecule for CVD of a specific metal are complex and depend on the application being considered. High-purity, dense metal films with controlled crystallite size and smooth surfaces deposited at relatively low temperatures ( $< 500^\circ\text{C}$ ), high deposition rates ( $> 0.1\ \mu\text{m}/\text{min}$ ) and low pressures are required for microelectronic applications. Some of these constraints may be relaxed in other coating applications where, for example, high substrate temperatures can be tolerated or impurities



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are not detrimental. As an example, glass coating processes generally require higher rates than microelectronic processes, but are often carried out at temperatures of 500–600 °C and at atmospheric pressure.

Precursors for CVD of metals can be broadly classified into three types: inorganic precursors, which do not contain carbon; metal-organic precursors, which contain organic ligands, but do not possess metal–carbon bonds; and organometallic precursors, which possess organic ligands and metal–carbon bonds. Precursors that have been used for the CVD of metals are classified in Tables 1 and 2 according

Table 1. Precursors used for CVD of metals listed alphabetically by element.

Molecular Precursor	Compound	Reference
<b>Ag</b> <sup>13</sup>	Ag(trifluoroacetate)	14
	Ag(acetate)	15
	Ag(neodecanoate)	16
	Ag(C <sub>4</sub> F <sub>7</sub> )	17
	Ag(acac)	14
	(Alkene)Ag(acac)	18
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Ag(PR <sub>3</sub> )	19
<b>Al</b> <sup>9</sup>	AlMe <sub>3</sub>	20,21
	AlEt <sub>3</sub>	22–26
	Al( <i>i</i> -Bu) <sub>3</sub>	27,28
	AlEt <sub>2</sub> Cl	22,24,29–33
	AlMe <sub>2</sub> H	34–45
	AlH <sub>3</sub> •NMe <sub>3</sub>	46–51
	AlH <sub>3</sub> •NEt <sub>3</sub>	52–54
	AlH <sub>3</sub> •NMe <sub>2</sub> Et	55,56
	AlH <sub>2</sub> (BH <sub>4</sub> )•NMe <sub>3</sub>	57
	Al(BH) <sub>3</sub> •NMe <sub>3</sub>	57
<b>Au</b> <sup>13</sup>	Me <sub>2</sub> Au(hfac)	58–64
	Me <sub>2</sub> Au(tfac)	65
	Me <sub>2</sub> Au(acac)	65
	MeAuPMe <sub>3</sub>	66
	Me <sub>3</sub> AuPMe <sub>3</sub>	20,130
	CF <sub>3</sub> AuPMe <sub>3</sub>	67
	(CF <sub>3</sub> ) <sub>3</sub> AuPMe <sub>3</sub>	67
	[(CF <sub>3</sub> ) <sub>2</sub> Au(OSiMe <sub>3</sub> )] <sub>2</sub>	68
	MeAu(CNMe)	66
<b>Co</b> <sup>69</sup>	CoCl <sub>2</sub>	70,71
	Co <sub>2</sub> (CO) <sub>8</sub>	72–74
	Co <sub>4</sub> (CO) <sub>12</sub>	75
	Co(CO) <sub>3</sub> (NO)	76
	HCo(CO) <sub>4</sub>	73,74
	CF <sub>3</sub> Co(CO) <sub>4</sub>	77
	Co(acac) <sub>2</sub>	78,79
	Co( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	77
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Co(CO) <sub>2</sub>	77
<b>Cr</b> <sup>69</sup>	CrF <sub>2</sub>	80
	CrCl <sub>2</sub>	81
	Cr(CO) <sub>6</sub>	82–85
	( $\eta^6$ -C <sub>7</sub> H <sub>8</sub> )Cr(CO) <sub>2</sub>	86
	Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	87,88
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cr(CO) <sub>3</sub> H	89
	Cr(N- <i>i</i> -Pr) <sub>2</sub>	89
	Cr(CH <sub>2</sub> CMe <sub>3</sub> ) <sub>4</sub>	89
	Cr(cumene) <sub>2</sub>	87,88

Table 1. (Continued)

<b>Cu</b> <sup>90,91</sup>	Cu(hfac) <sub>2</sub>	92–105
	Cu(tfac)	106
	Cu(acac) <sub>2</sub>	107–110
	Cu(dpm) <sub>2</sub>	98
	Cu(ppm) <sub>2</sub>	98
	Cu(fod) <sub>2</sub>	94
	Cu(acim) <sub>2</sub>	111
	Cu(acen)	111
	Cu(nona-F) <sub>2</sub>	112
	( $\beta$ -diketonate)CuPR <sub>3</sub>	113–120
	( $\beta$ -diketonate)Cu(1,5-COD)	115,120–124
	(hfac)Cu(VTMS)	125–132
	(hfac)Cu(CO)	133
	(hfac)Cu(alkyne)	115,120,134–136
	(hfacCu) <sub>2</sub> cyclooctatetraene	4
	(hfac)Cu(1,3-butadiene)	4
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cu(PR <sub>3</sub> )	137,138
	( <i>t</i> -BuO)Cu(PMe <sub>3</sub> )	137
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cu(CN- <i>t</i> -Bu)	3
<b>Fe</b> <sup>69</sup>	[Cu(O- <i>t</i> -Bu)] <sub>4</sub>	139
	Cu(O- <i>t</i> -Bu)(OR <sub>F</sub> )	5
	FeF <sub>3</sub>	140
	Fe(CO) <sub>5</sub>	141,142
<b>Ir</b> <sup>69</sup>	[ $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ]Fe(CO) <sub>2</sub> ] <sub>2</sub>	143
	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	77,144
<b>Hf</b> <sup>69</sup>	HfI <sub>4</sub>	145
<b>Ir</b> <sup>69</sup>	IrF <sub>6</sub>	146
	IrCl <sub>3</sub>	146
	Ir(allyl) <sub>3</sub>	147,148
	(acac)Ir(1,5-COD)	149
	[(MeO)Ir(1,5-COD)] <sub>2</sub>	149
	Ir(acac) <sub>3</sub>	150
	IrCl <sub>4</sub>	146
	IrBr <sub>3</sub>	146
	(MeC <sub>5</sub> H <sub>4</sub> )Ir(1,5-COD)	151
	(C <sub>5</sub> H <sub>5</sub> )Ir(1,5-COD)	151
<b>Mn</b> <sup>69</sup>	[(1,5-COD)Ir(OAc)] <sub>2</sub>	151
	Mn <sub>2</sub> (CO) <sub>10</sub>	152–154
<b>Mo</b> <sup>69</sup>	Mn( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	155
<b>Mo</b> <sup>69</sup>	MoF <sub>6</sub>	156
	MoCl <sub>5</sub>	157–163
	Mo(CO) <sub>6</sub>	82–85,157,164–168
	(Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub> )Mo(CO) <sub>3</sub>	149
	( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mo(CO) <sub>3</sub>	149
	Mo(allyl) <sub>4</sub>	169
<b>Nb</b> <sup>69</sup>	NbCl <sub>5</sub>	168,170–180
	NbBr <sub>5</sub>	168,170–180
<b>Ni</b> <sup>181</sup>		
	Ni(CO) <sub>4</sub>	94,182,183
	Ni( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	184
	Ni( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub>	185
<b>Os</b> <sup>69</sup>		
	OsCl <sub>4</sub>	186
	Os(hfb)(CO) <sub>4</sub>	187

Table 1. (Continued)

<b>Pd</b> <sup>181</sup>	Pd(allyl) <sub>2</sub>	188
	Pd(Meallyl) <sub>2</sub>	188
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Pd(allyl)	188
<b>Pt</b> <sup>181</sup>	Pt(CO) <sub>2</sub> Cl <sub>2</sub>	189
	Pt(acac) <sub>2</sub>	189
	Pt(PF <sub>3</sub> ) <sub>4</sub>	189,190
	PtMe <sub>2</sub> (MeNC) <sub>2</sub>	191-193
	(1,5-COD)PtMe <sub>2</sub>	191-193
	(1,5-COD)PtMe( $\eta^1$ -C <sub>5</sub> H <sub>5</sub> )	191-193
	(1,5-COD)PtMeCl	191-193
	(C <sub>5</sub> H <sub>5</sub> )PtMe(CO)	191-193
	(C <sub>5</sub> H <sub>5</sub> )Pt(allyl)	191-193
	(acac)PtMe <sub>3</sub>	191-193
	(C <sub>5</sub> H <sub>5</sub> )PtMe <sub>3</sub>	194-197
	(C <sub>5</sub> H <sub>4</sub> Me)PtMe <sub>3</sub>	194-197
	Pt(hfac) <sub>2</sub>	198-201
<b>Re</b> <sup>69</sup>	ReF <sub>6</sub>	202-205
	ReCl <sub>5</sub>	203
	Re <sub>2</sub> (CO) <sub>10</sub>	206-208
	HRe(CO) <sub>5</sub>	185
<b>Rh</b> <sup>69</sup>	[(PF <sub>3</sub> ) <sub>2</sub> RhCl] <sub>2</sub>	209
	Rh( $\eta^3$ -allyl) <sub>3</sub>	147,148,210-213
	(acac)Rh(CO) <sub>2</sub>	147,211,214
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	215
	Rh(tfac) <sub>3</sub>	216
	Rh <sub>2</sub> Cl <sub>2</sub> (CO) <sub>4</sub>	213
	Rh( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub>	213
	Rh( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(1,5-COD)	213
	Rh( $\eta^5$ -allyl)(CO) <sub>2</sub>	213
<b>Ru</b> <sup>69</sup>	Ru <sub>3</sub> (CO) <sub>12</sub>	217
	Ru(hfb)(CO) <sub>4</sub>	187
	Ru( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	217,218
	Ru(acac) <sub>2</sub>	217
<b>Ta</b> <sup>69</sup>	TaCl <sub>5</sub>	145,162,219-223
	TaF <sub>5</sub>	224
	Ta(CO) <sub>5</sub>	149
<b>Ti</b> <sup>69</sup>	TiI <sub>4</sub>	225
	TiBr <sub>4</sub>	226
	TiCl <sub>4</sub>	227
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiR <sub>2</sub>	228-231
	"( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti"	232
	( $\eta^7$ -C <sub>7</sub> H <sub>7</sub> )Ti( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )	233,234
<b>V</b> <sup>69</sup>	VI <sub>4</sub>	217
	VCl <sub>4</sub>	235
	$\eta^5$ -C <sub>5</sub> H <sub>5</sub> V(CO) <sub>4</sub>	217

Table 1. (Continued)

<b>W</b> <sup>236</sup>	WF <sub>6</sub>	237-251
	WCl <sub>6</sub>	252-257
	WBr <sub>6</sub>	258
	W(PF <sub>3</sub> ) <sub>6</sub>	165,259,260
	W(CO) <sub>6</sub>	165,253,261-264
	W( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	170,265
	W( $\eta^4$ -C <sub>4</sub> H <sub>6</sub> ) <sub>3</sub>	266
	W( $\eta^3$ -allyl) <sub>4</sub>	267
	W(C <sub>4</sub> H <sub>6</sub> O) <sub>3</sub>	268
	W( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> CH <sub>3</sub>	269
	W( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> H	270
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> WH <sub>2</sub>	271,272
	( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> WH <sub>2</sub>	271
	(1,5-COD)W(CO) <sub>4</sub>	270
<b>Zr</b> <sup>69</sup>	( $\eta^6$ -C <sub>7</sub> H <sub>8</sub> )W(CO) <sub>3</sub>	270
	ZrI <sub>4</sub>	273
	ZrBr <sub>4</sub>	220
	Zr(CH <sub>2</sub> - <i>t</i> -Bu) <sub>4</sub>	228-231,274

Table 2. Precursors used for CVD of metals listed by ligand type.

Molecular Precursor	Compound	Reference
<b>Inorganic Precursors</b> <b>Metal Halides</b>	TiI <sub>4</sub>	225
	TiBr <sub>4</sub>	275
	ZrI <sub>4</sub>	273
	ZrBr <sub>4</sub>	220
	HfI <sub>4</sub>	145
	VI <sub>2</sub>	217
	VCl <sub>4</sub>	235
	NbCl <sub>5</sub>	168,170-180
	NbBr <sub>5</sub>	168,170-180
	TaCl <sub>5</sub>	145,162,219-223
	TaF <sub>5</sub>	224
	CrF <sub>2</sub>	80
	CrCl <sub>2</sub>	81
	MoF <sub>5</sub>	156
	MoCl <sub>5</sub>	157-163
	WF <sub>6</sub>	237-251
	WCl <sub>6</sub>	252-257
	WBr <sub>6</sub>	258
	ReF <sub>6</sub>	202-205
	ReCl <sub>5</sub>	203
<b>Metal-organic Precursors</b> <b>Metal <math>\beta</math>-Diketonates</b>	FeF <sub>3</sub>	140
	OsCl <sub>4</sub>	186
	CoCl <sub>2</sub>	70,71
	[(PF <sub>3</sub> ) <sub>2</sub> RhCl] <sub>2</sub>	209
	IrCl <sub>4</sub>	146
	IrBr <sub>3</sub>	146
	IrF <sub>6</sub>	146
	IrCl <sub>3</sub>	146
	Ru(acac) <sub>2</sub>	217
	Co(acac) <sub>2</sub>	70,71
	Rh(tfac) <sub>3</sub>	216
	Ir(acac) <sub>3</sub>	150
	(acac)Rh(CO) <sub>2</sub>	147,211,214

Table 2. (Continued).

	(acac)Ir(1,5-COD)	149
	Pt(acac) <sub>2</sub>	198-201
	Pt(hfac) <sub>2</sub>	198-201
	(acac)PtMe <sub>3</sub>	191-193
	Cu(tfac) <sub>2</sub>	106
	Cu(acac) <sub>2</sub>	107-110
	Cu(dpm) <sub>2</sub>	98
	Cu(fod) <sub>2</sub>	98
	Cu(acim) <sub>2</sub>	111
	Cu(acen)	111
	Cu(ppm) <sub>2</sub>	98
	(hfacCu) <sub>2</sub> cyclooctatetraene	4
	Ag(acac)	14
	(alkene)Ag(acac)	18
	Me <sub>2</sub> Au(hfac)	58-64
	Me <sub>2</sub> Au(tfac)	65
	Me <sub>2</sub> Au(acac)	65
	(β-diketonate)CuPR <sub>3</sub>	113-120
	(β-diketonate)Cu(olefin)	115,120-132
	(β-diketonate)Cu(alkyne)	115,120,134-136
<b>Metal β-Ketoimines</b>	Cu(nona-F) <sub>2</sub>	112
	(β-ketoimine)CuL	119
<b>Metal Hydrides</b>	Trimethylamine alane (TMAA)	46-51
	Triethylamine alane (TEAA)	52-54
	Dimethylethylamine alane (DMEAA)	55,56
	Trimethylamine aluminaborane (TMAAB)	57
<b>Metal Alkoxides</b>	( <i>t</i> -BuO)Cu(PMe <sub>3</sub> )	137
	[Cu(O- <i>t</i> -Bu)] <sub>4</sub>	139
	Cu(O- <i>t</i> -Bu)(OR <sub>F</sub> )	5
<b>Metal Amides</b>	Cr(N- <i>i</i> -Pr) <sub>2</sub>	89
<b>Metal Carboxylates</b>	(1,5-COD)Ir(OAc) <sub>2</sub>	151
	Ag(trifluoroacetate)	14
	Ag(acetate)	15
	Ag(neodecanoate)	16
<b>Organometallic Precursors</b>		
<b>Metal Alkyls</b>	Zr(CH <sub>2</sub> - <i>t</i> -Bu) <sub>4</sub>	276
	Cr(CH <sub>2</sub> CMMe <sub>3</sub> ) <sub>4</sub>	89
	Co(CO) <sub>4</sub>	73,74,77
	CF <sub>3</sub> Co(CO) <sub>4</sub>	77
	(1,5-COD)PtMe <sub>2</sub>	191-193
	(1,5-COD)PtMe(η <sup>1</sup> -C <sub>5</sub> H <sub>5</sub> )	191-193
	CF <sub>3</sub> AuPMe <sub>3</sub>	67
	(CF <sub>3</sub> ) <sub>3</sub> AuPMe <sub>3</sub>	67
	[(CH <sub>3</sub> ) <sub>2</sub> Au(OSiMe <sub>3</sub> )] <sub>2</sub>	68
	MeAuCNMe	66
	MeAuPMe <sub>3</sub>	66
	Me <sub>3</sub> AuPMe <sub>3</sub>	67
	Trimethylaluminum (TMA)	20,21
	Triethylaluminum (TEA)	22-26
	Triisobutylaluminum (TIBA)	27,28
	Diethylaluminum chloride (DEACl)	22,24,29-33
	Dimethylaluminum hydride (DMAH)	34-45
<b>Metal Alkenes</b>	(hfac)Cu(alkene)	125-132
	(1,5-COD)W(CO) <sub>4</sub>	270
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	215
<b>Metal Alkyls</b>	Mo(η <sup>3</sup> -allyl) <sub>4</sub>	267
	W(η <sup>3</sup> -allyl) <sub>4</sub>	267
	Rh(η <sup>3</sup> -allyl) <sub>3</sub>	147,148,210-213
	Ir(η <sup>3</sup> -allyl) <sub>3</sub>	185
	Pd(η <sup>3</sup> -allyl) <sub>2</sub>	6
	Pd(η <sup>3</sup> -methylallyl) <sub>2</sub>	6

Table 2. (Continued).

<b>Metal Carbonyls</b>	Ta(CO) <sub>5</sub>	149
	Cr(CO) <sub>6</sub>	82-85
	Mo(CO) <sub>6</sub>	82-85,157,164-168
	W(CO) <sub>6</sub>	165,253,261-264
	Mn <sub>2</sub> (CO) <sub>10</sub>	152-154
	Re <sub>2</sub> (CO) <sub>10</sub>	206-208
	HRe(CO) <sub>5</sub>	185
	Fe(CO) <sub>5</sub>	141,142
	Ru <sub>3</sub> (CO) <sub>12</sub>	217
	Ru(hfb)(CO) <sub>4</sub>	187
	Co <sub>2</sub> (CO) <sub>8</sub>	72-74
	Co <sub>4</sub> (CO) <sub>12</sub>	75
	HCo(CO) <sub>4</sub>	73,74
	CF <sub>3</sub> Co(CO) <sub>4</sub>	77
	Ni(CO) <sub>4</sub>	94,182,183
<b>Metalloenes</b>	"Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	232
	Fe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	77,144
	Ru(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	217,218
	Co(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	77
	Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	184
	Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub>	185
<b>Cyclopentadienyl compounds</b>	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )V(CO) <sub>4</sub>	217
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Cr(CO) <sub>3</sub> H	89
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )W(CO) <sub>3</sub> X	269-277
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> WH <sub>2</sub>	271,272
	(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> WH <sub>2</sub>	271
	[(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> ] <sub>2</sub>	143
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Co(CO) <sub>2</sub>	77
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	215
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	215
	(η <sup>5</sup> -MeC <sub>5</sub> H <sub>4</sub> )Ir(1,5-COD)	151
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Ir(1,5-COD)	151
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )PtMe(CO)	191-193
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Pt(allyl)	191-193
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )PtMe <sub>3</sub>	6,194-196
	(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me)PtMe <sub>3</sub>	6,194-196
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Cu(PMe <sub>3</sub> )	137,278
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Cu(CN- <i>t</i> -Bu)	3
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Cu(PR <sub>3</sub> )	137,138
	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Ag(PR <sub>3</sub> )	19
<b>Metal Arenes</b>	Cr(η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	87,88
	(η <sup>6</sup> -C <sub>7</sub> H <sub>8</sub> )Cr(CO) <sub>3</sub>	86
	Cr(cumene) <sub>2</sub>	87,88
	(η <sup>6</sup> -Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub> )Mo(CO) <sub>3</sub>	149
	(η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> )Mo(CO) <sub>3</sub>	149
	W(η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	170,265
	[(MeO)Ir(1,5-COD)] <sub>2</sub>	149

to the identity of the central metal atom and the type of the supporting ligands, respectively. This list is not meant to be comprehensive but provides an indication of the types of compounds used, which metals have been studied, and some leading references for the reader to retrieve more information.<sup>[13-278]</sup> A list of the abbreviations used in this article is given in Table 3.

There are a number of obvious precursor design requirements that ideally must all be satisfied for successful CVD of a metal film. The most important precursor attributes and consequences can be summarized as follows: high vapor



Table 3. List of abbreviations.

1,5-COD	1,5-cyclooctadiene
BTMSA	bis(trimethylsilyl)acetylene
Cp	cyclopentadienyl
DEACl	diethylaluminum chloride
DIBAH	diisobutylaluminum hydride
DMAH	dimethylaluminum hydride
DMEAA	dimethylethylaminealane
Hdpm	dipivaloylmethane
Et	ethyl
acac	acetylacetonato
acim	4-imino-2-pentanato
dpm	2,2,6,6-tetramethyl-3,5-heptanedionato
fod	2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato
H(hfac)	1,1,1,5,5,5-hexafluoro-2,4-pentanedione or 1,1,1,5,5,5-hexafluoroacetylacetonato
hfac	1,1,1,5,5,5-hexafluoroacetylacetonato
pentanone	
nona-F	1,1,1,5,5,5-hexafluoro-4-[(2,2,2-trifluoroethyl)imino]-2-pentanedionato
ppm	6,6,7,7,7-pentafluoro-2,2-dimethyl-3,5-heptanedionato
tdf	1,1,1,2,2,3,3,7,7,8,8,9,9-tetradecafluoro-4,6-nonanedionato
tfac	trifluoroacetylacetonato
acen	4,4'-(1,2-ethanediyldinitrilo)bis(2-pentanedionato)
hfb	hexafluoro-2-butene
HMDS	hexamethyldisilazane
<i>i</i> -Bu	iso-butyl
<i>i</i> -Pr	iso-propyl
Me	methyl
NBD	norbornadiene
Np	neopentyl
PTFE	poly(tetrafluoroethylene)
<i>t</i> -Bu	tertiary butyl
TEA	triethylaluminum
TEAA	triethylaminealane
TIBA	triisobutylaluminum
TMA	trimethylaluminum
TMAA	trimethylaminealane
tmhd	2,2,6,6-tetramethyl-3,5-heptanedionato
VTMS	vinyltrimethylsilane

pressures, to achieve high transport rates; careful precursor design, to control the surface reaction of the precursor to give high purity films; thermally inert precursors at the delivery temperature, to avoid premature decomposition; and liquid precursors, to ensure reproducible delivery rates if standard delivery methods are used.

### 3.1. Volatility

Traditional methods of precursor delivery to CVD reactors often rely on evaporation of the precursor at a given temperature to an extent limited by its equilibrium vapor pressure. Therefore, high vapor pressures are required to allow convenient delivery of precursors into CVD reactors and to achieve high deposition rates. High vapor pressures are favored by low molecular weight and a low degree of molecular aggregation, with monomeric species being the most desirable species. Inorganic complexes often exhibit low vapor pressures as a result of aggregation. This is exemplified by the vapor pressure data shown in Table 4 and Figure 2, which demonstrate that although the formula weight of  $\text{SnCl}_2$  is lower than that of  $\text{SnCl}_4$ , the vapor pressure of  $\text{SnCl}_4$  is higher because the tin center is more coordi-

Table 4. Temperatures at which vapor pressures [mmHg] are obtained for a variety of inorganic and metal-organic compounds.

Compound	Temperature in °C						
	1 mm	10 mm	40 mm	100 mm	400 mm	760 mm	m.p.
$\text{MoF}_6$	-65.5	-40.8	-22.1	-8.0	17.2	36.0	17.0
$\text{WF}_6$	-71.4	-49.2	-33.0	-20.3	1.2	17.3	-0.5
$\text{TiCl}_4$	-13.9	21.3	48.4	71.0	112.7	136.0	-30.0
$\text{SnCl}_4$	-22.7	10.0	35.2	54.7	92.1	113.0	-30.2
$\text{Ni}(\text{CO})_4$	---	---	-23.0	-6.0	25.8	42.5	-25.0
$\text{Fe}(\text{CO})_5$	---	4.6	30.3	50.3	86.1	105.1	-21.0
$\text{Cr}(\text{CO})_6$	36.0	68.3	91.2	108.0	137.2	151.0	---
$\text{Co}(\text{CO})_3\text{NO}$	---	---	11.0	29.0	62.0	80.0	-11.0
$\text{SnCl}_2$	316.0	391.0	450.0	493.0	577.0	623.0	246.8

natively saturated and therefore exhibits a lower tendency towards aggregation compared to  $\text{SnCl}_2$ . There are exceptions to this trend where the metal halides exist in high oxidation states ( $\text{WF}_6$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ) which also leads to relatively high coordination numbers, thereby reducing the tendency for oligomerization. As an example, the vapor pressure of  $\text{WF}_6$  at room temperature is 1000 torr, allowing the use of mass flow controllers for precursor delivery.

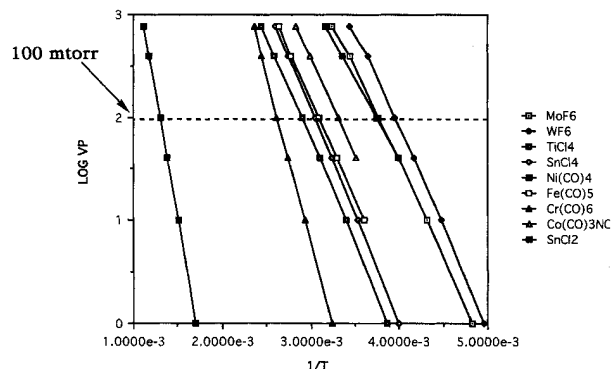


Fig. 2. Vapor pressure for compounds identified in Table 4.

Aggregation can also be a problem for metal-organic and organometallic complexes, although the use of multidentate chelating ligands such as  $\beta$ -diketonates can help alleviate such problems. For these compounds, the formula weights are often higher than for inorganic precursors as a result of the presence of the organic ligands, leading to relatively low volatility. However, these complexes are more easily derivatized to alter volatility and melting point than inorganic compounds. When comparing the volatility of metal-containing compounds, it is important to define the *molecular* formula rather than the *empirical* formula. For example, it may appear surprising that " $\text{Al}(\text{i-Bu})_2\text{H}$ " is not more volatile than " $\text{Al}(\text{i-Bu})_3$ ". However, inspection of the *molecular* formulae reveals that  $[\text{Al}(\text{i-Bu})_2\text{H}]_3$  is trimeric and has a relatively high molecular weight while  $\text{Al}(\text{i-Bu})_3$  is monomeric and has a relatively low molecular weight.

In general, the low vapor pressures of many metal-organic compounds cause a serious limitation to the CVD of metal

films where traditional methods of precursor delivery, such as passing a gas through a bubbler containing the solid precursor, are employed, and make it difficult to interpret the data from feed-rate-limited CVD (see Section 5). Although vapor pressure can be increased by increasing the temperature, the precursor often begins to decompose, which also leads to irreproducible delivery rates and the transport of unknown species. This is a problem, for example, with Cu precursors, where vapor pressures are typically in the 10–100 mtorr range. However, this limitation can be avoided by using alternative delivery methods such as aerosol delivery and/or liquid delivery. These approaches rely on evaporation of the precursor from aerosol droplets in a carrier gas or from a solution sprayed onto a hot surface, therefore allowing the precursor to be kept at or even below room temperature until it is rapidly vaporized. While this approach has been used for a variety of materials,<sup>[279–281]</sup> it has not been used extensively for CVD of metals.<sup>[282–284]</sup>

## 3.2. Reaction Pathways

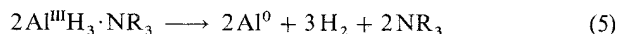
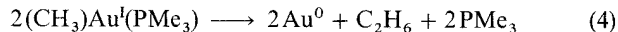
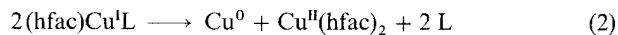
The reaction pathway for a precursor determines the purity of the deposited film and the deposition rate. In some cases, the reaction pathway can be modified by changing the nature of the ligands to give a pathway that deposits higher purity material at higher rates and, if desired, at lower temperatures, as discussed below. It is important to note that rates are often limited by the precursor vapor pressure, which suggests that synthesis of precursors with higher vapor pressures is an important goal. This is particularly crucial for classes of CVD precursors that already decompose at low temperatures but which have relatively low vapor pressures. Examples include most of the precursors for Cu, Pt, Pd, Ru, Co, Au, Ag, and many of the other metals in Table 1.

Inorganic precursors such as metal halides typically do not produce pure metal films below approximately 600 °C and generally require the presence of a reducing agent such as H<sub>2</sub> or SiH<sub>4</sub> to avoid halide contamination. Furthermore, they are often solids at the source temperature (with several important exceptions, such as WF<sub>6</sub>, IrF<sub>6</sub>, SnCl<sub>4</sub>, and TiCl<sub>4</sub>), which makes delivery into the reactor more difficult to control compared to liquid precursors. However, given these drawbacks, high-purity films can be deposited at high rates, and the precursors are generally inexpensive, easily purified, and commercially available. Therefore, metal halides are often the optimum precursors within the constraints described above, as is currently the case for WF<sub>6</sub> (see Eq. 1). This is often the case for applications such as solar and wear-resistant coatings, where low cost is often the highest priority and high deposition temperatures can be tolerated.



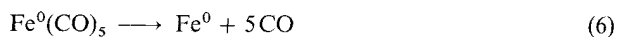
In contrast, metal-organic and organometallic precursors have the advantages (over inorganic precursors) that they

often thermally decompose at lower temperatures, usually have higher vapor pressures, and are more often liquids, which can simplify precursor delivery. They have the disadvantage that impurity incorporation (C, O, F, P) is common, and to obtain pure films, they often require a reducing agent such as H<sub>2</sub> or H<sub>2</sub>O, or an oxidizing agent such as O<sub>2</sub>. The problem of impurity incorporation is particularly difficult for reactive metals, such as Cr and Ti, for which no good organometallic or metal-organic precursors currently exist.<sup>[285, 286]</sup> However, there are many examples where high-purity metal films have been deposited from these classes of precursors without any co-reactant (such as a reducing agent). This requires a decomposition mechanism where the organic ligands are removed from the reaction chamber intact or in which a reaction pathway exists to form volatile products which desorb easily from the surface. Cases where this occurs are the disproportionation of copper(I) compounds,<sup>[121, 127, 128, 135, 287, 288]</sup> the  $\beta$ -hydride elimination of Al(*i*-Bu)<sub>3</sub>,<sup>[27]</sup> homolysis of Au–C bonds in (CH<sub>3</sub>)Au(PMe<sub>3</sub>),<sup>[289–292]</sup> and the use of precursors such as AlH<sub>3</sub>·NR<sub>3</sub> which do not contain metal–carbon bonds.<sup>[8]</sup> Examples of these reactions are given in Equations 2–5.



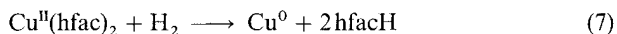
The well-known  $\beta$ -hydride elimination is an example of a mechanism which cleaves the metal–carbon bond. However, because this may involve liberation of organic radicals as reactive intermediates (for example, isobutyl radicals on an Al surface), alternative reactions can occur that lead to impurity incorporation (e.g.,  $\beta$ -methyl group elimination in the case of Al CVD from Al(*i*-Bu)<sub>3</sub>).<sup>[27]</sup> For this reason, alternative precursors for the CVD of Al have been sought, and the Lewis base adducts of AlH<sub>3</sub> provide a viable method to deposit high-purity Al films from precursors that are unlikely to produce C-contaminated films because the precursor does not contain Al–C bonds.

Overall, rough guidelines can be derived for choosing the organic portion of a organometallic precursor. As the metal–carbon bond order increases (metal alkene  $\approx$  metal alkyne  $\leq$  metal alkyl  $<$  metal ( $\eta^3$ -allyl)  $<$  metal carbonyl  $<$  metal cyclopentadienyl  $<$  metal arene) in organometallic compounds, the chances for carbon incorporation are increased due to the increased strength of M–C bonding. For example, CVD of Fe using Fe(CO)<sub>5</sub> (see Eq. 6) gives rise to relatively pure films compared to Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (in the absence of H<sub>2</sub>).<sup>[293]</sup>



In general, the more noble (later or further to the right) the metal and the lower it is in a given group in the periodic table, the more easily it is reduced, the less stable the M–X bonds, and the less the likelihood of C incorporation. For example, Ni(CO)<sub>4</sub> gives rise to purer metal films than transition metal carbonyl compounds earlier in the first row of the transition metal series in the periodic table. Furthermore, films derived from Pd, Pt, Cu, and Ag cyclopentadienyl complexes have lower C incorporation than films derived from cyclopentadienyl complexes of metals earlier in the periodic table. However, these trends can be modified by the details of the reaction mechanism, which varies depending on the metal and ligands involved.

In the absence of an appropriate reaction pathway, organometallic and metal-organic precursors often give rise to impurity incorporation, particularly C and O, as is apparent from a review of the CVD of many transition metals. Impurity incorporation can be avoided in certain cases by the addition of a reducing agent (e.g., H<sub>2</sub>) or an oxidizing agent to remove the organic ligands. For example, the reduction of metal carbonyl compounds by H<sub>2</sub> produces pure metal films due to Fischer–Tropsch type catalysis chemistry.<sup>[294]</sup> Metal β-diketonates are popular choices as precursors mainly because the fluorinated derivatives exhibit high vapor pressures and are generally capable of high transport rates. However, the presence of a reducing agent such as H<sub>2</sub> is generally required in order to avoid extensive contamination in the film; for example, the CVD of high-purity copper films has been achieved by reduction of Cu(hfac)<sub>2</sub> with H<sub>2</sub> (Eq. 7). For reactive metals such as Ti, however, even the use of a hydrogen plasma does not provide sufficiently reducing conditions to form pure metal films from organometallic precursors such as Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub>).



An example of the use of an oxidizing agent such as oxygen is CVD of Ir from (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ir(1,5-COD).<sup>[295]</sup> The formation of pure metal films in the presence of O<sub>2</sub> is only likely to occur where the metal forms an oxide that is thermodynamically unstable with respect to formation of the metal at the deposition temperature such that only the carbon-containing ligands are oxidized to CO. Reactions catalyzed by the metal surface, such as Wacker-type processes, are likely under these conditions.<sup>[294]</sup>

#### 4. Hot- and Cold-Wall Reactors

Chemical vapor deposition of metals has been carried out in many types of reactors, primarily hot- and cold-wall reactors, and, in some cases, plasma reactors.<sup>[296–298]</sup> An account of the characteristics of hot- and cold-wall reactors is relevant to this discussion for two reasons. First, the type of reactor and its operating conditions can have a profound affect on the deposition process and, second, the mode of

reactor operation can be used to advantage to derive quantitative information if care is taken in interpretation of rate data as described below.

Hot-wall reactors have been used extensively for laboratory studies of metal CVD, even though most metal CVD in industry is carried out in single-wafer, cold-wall systems. The advantages of hot-wall systems are that they are simple to operate, can accommodate several substrates, can be operated under a range of pressures and temperatures, and allow different orientations of the substrate relative to the gas flow. The major problem with hot-wall systems is that deposition can occur not only on the substrate but also on the reactor walls. These deposits can eventually fall off the surface and contaminate the substrate. Also, the correspondingly large consumption of the precursor can result in feed-rate-limited deposition (discussed below) at relatively low temperatures compared to cold-wall reactors. Deposition only on the substrate can occur in special cases when deposition is selective and the reactant does not decompose on the reactor walls.<sup>[113, 115]</sup> However, reactions usually occur on the walls, and in most cases the fraction of the surface area of the reactor covered with deposit can change with time during an experiment and from one experiment to another, leading to problems in reproducing deposition conditions. In addition, homogeneous gas-phase reactions in the heated gas can occur, which can lead to reduced deposition rates. For this reason, hot-wall reactors are used primarily at the laboratory scale to study the overall viability of using a given precursor for CVD. They are also often used to determine reaction-product distributions because the large heated surface area can consume the precursor completely and provide high yields of the reaction products.<sup>[113, 115]</sup> Although some exceptions exist, hot-wall reactors are generally not used in industry or for quantitative measurements of reaction kinetics for CVD of metals. They are, however, used extensively in industry for CVD of semiconductors and oxides, where precursors with much higher vapor pressures are available.

On the other hand, cold-wall reactors are used extensively at the laboratory scale and are also the industry workhorse for CVD of metals. Cold-wall reactors usually accommodate only a single wafer in various orientations to the flow, but pressure and temperature can be controlled, plasmas can be used, deposition does not occur on the reactor walls, homogeneous reactions can occur only over a smaller volume of the reactor above the heated substrate, and higher deposition rates can be obtained than with hot-wall reactors. Cold-wall reactors are also more suitable for studies of selective deposition because deposition does not occur on the reactor walls. They are also used for measurements of kinetic parameters because surface-reaction-limited kinetics can be achieved easily.<sup>[121, 127, 135]</sup> To obtain kinetic data, it is desirable to operate in the differential mode, where the conversion of the precursor is low enough to ensure surface-reaction-limited kinetics and to minimize the partial pressures of the reaction products.<sup>[127]</sup> Because deposition occurs only on a single substrate so that the precursor con-

sumption rate is low, high deposition rates can be obtained. For manufacturing applications, single-wafer cold-wall reactors are preferred because they allow better control of deposition behavior.

## 5. Influence of Reactor Operating Conditions on Film Growth

It is important to understand the behavior of CVD reactors to interpret rate measurements obtained with new precursors and to determine how to design and operate CVD reactors for established precursors. A variety of measurements are typically made when studying new and existing precursors, but one of the simplest is the dependence of the deposition rate on the substrate temperature (even though this measurement is often not made). The temperature dependence of the deposition rate can reflect the kinetics of the surface reactions (but only under surface-reaction-limited deposition). A somewhat more sophisticated measurement is the dependence of the rate on the reactant partial pressure. However, this measurement is usually not done for new precursors and is difficult to carry out for precursors with low vapor pressures, where only a narrow range of low pressures can be utilized. Insight into the surface reaction mechanisms may allow synthesis of new precursors or modification of operating conditions to provide new reaction pathways for increased deposition rates. The deposition rate has been measured as a function of temperature for only a very small fraction of the precursors in Table 1. The rate as a function of precursor partial pressure has been measured only for an even smaller number of the precursors, usually for established precursors such as  $\text{Al}(i\text{-Bu})_3$ ,  $\text{Cu}(\text{hfac})_2$ ,  $\text{MoCl}_5$ , and  $\text{WF}_6$ .

A problem with rate measurements is that they can give complex information which can be difficult to interpret. Even where kinetic data have been obtained it is often not clear whether this information can be attributed to an elementary step or a combination of elementary reactions. In addition, complex variations of the rate with changes in the temperature and reactant partial pressure are observed even under surface-reaction-limited conditions. An example is CVD of Cu from  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  precursors.<sup>[90, 91, 127]</sup> A further complication is that these variations are not necessarily directly related to the reactions occurring on the substrate if the deposition is feed-rate limited or transport-rate limited. Another complication is that various types of reactors have been used for CVD of metals. Because of differences in geometry, reactant introduction, and other factors, different results are often obtained for the same precursor, making it difficult to compare results.

The following narrative discusses rate measurements from CVD reactors and attempts to show when measurements are made under conditions in which the actual kinetics attributable to the precursor are observed. The motivation for this is that measurements have been reported under a wide

variety of conditions and it is usually not clear when the deposition is surface-reaction, feed-rate, or transport-rate limited. This distinction is critical if the data are to be used to assist in precursor design. It must be emphasized that the idea of different operating regimes is a simplification; reactors often operate under conditions that are intermediate to two regimes, or the operating regime changes as relatively small changes are made in the operating conditions.

For conventional precursor delivery, the deposition process involves a series of three steps: a) introduction of precursor vapor, b) transport of precursor to the surface of the substrate, and c) surface reaction of the precursor. Because these steps are in series, the slowest step will limit the overall rate, and three cases are possible. For precursors with low vapor pressures step a often limits the rate, while for precursors with high vapor pressures, such as  $\text{WF}_6$ , the rate will often be limited by either step b or c. In terms of Figure 1, the feed rate and transport to the surface are contained in step 1 while step c corresponds to steps 2–6 in Figure 1.

The maximum deposition rate can be given by a simple expression from gas kinetic theory.

In Equation 8, rate [cm/s] is the deposition rate,  $\alpha$  (dimensionless) the fraction of reactant molecules that react after striking the surface,  $P_s$  [dynes/cm<sup>2</sup>] the precursor partial pressure immediately above the surface,  $v_m$  [cm<sup>3</sup>] the volume of depositing metal atom,  $m_t$  [g] the molecular mass of precursor,  $k_B$  Boltzmann's constant [ $1.38 \times 10^{-16}$  erg/(molecule K)],  $T$  [K] the temperature of gas above the substrate,  $a_0$  (dimensionless) a constant,  $E_A$  [erg/mol] the activation energy, and  $R$  [erg/(mol K)] the gas constant.

$$\text{rate} = \frac{\alpha P_s v_m}{\sqrt{2\pi m_t k_B T}} = \frac{\alpha_0 P_s v_m \exp[-E_A/(RT)]}{\sqrt{2\pi m_t k_B T}} \quad (8)$$

The parameter  $\alpha$  takes into account the details of the adsorption-desorption-reaction phenomena and depends exponentially on temperature. The maximum value of  $\alpha$  is 1 and is achieved when every collision results in reaction. This equation predicts that approximately 1 monolayer (roughly  $1 \text{ \AA}$  of metal) can be deposited every second at  $10^{-6}$  torr if  $\alpha = 1$ . At  $10^{-2}$  torr, 10000 monolayers per second and at 1 torr,  $10^6$  monolayers per second can be deposited. In most cases,  $\alpha \ll 1$ , and the actual deposition rate is much lower than the values mentioned above. The parameter  $\alpha$  is also important because values of  $\alpha$  near unity result in poor conformality.<sup>[1299]</sup> Conversely, values of  $\alpha$  much less than unity provide conformal deposition.

The value of  $\alpha$  can be controlled through precursor design. At a given temperature, precursors with lower decomposition temperatures will have higher values of  $\alpha$ . Therefore, conformality can be improved by using precursors that are more thermally inert but at the expense of lowering the deposition rate.

For diffusion-limited and feed-rate-limited deposition, the precursor pressure at the surface,  $P_s$ , can be much lower than

the pressure of the precursor in the delivery system. For this case, the deposition rate is reduced below the maximum possible value as discussed below.

### 5.1. Feed-Rate-Limited CVD

The case of feed-rate-limited deposition is often encountered for precursors with low vapor pressures under conditions where the reactant conversion is high. In this case, with no diffusion limitation, the local deposition rate is given by Equation 8. This is usually observed with low-pressure hot-wall reactors where diffusion is rapid but the surface area for reaction is large. This phenomenon can also occur in cold-wall reactors. For a given system and operating conditions, it can be determined whether the deposition rate is feed-rate limited by estimating the fraction of the precursor consumed by the reaction. This is accomplished by measuring the growth rate and the deposition area to get the total rate of precursor consumption by reaction. It is then compared to the rate at which the precursor is delivered into the reactor. If the fraction (precursor reacted/precursor introduced) is near unity, and little precursor exits the reactor, feed-rate-limited deposition is occurring.

Assuming all of the reactant decomposes on the heated area and assuming only one metal atom is present in each precursor molecule, the deposition rate is given by Equation 9.

$$\text{rate} = FM_m/(A\rho) \quad (9)$$

Here rate [cm/s] is the deposition rate,  $F$  [mol/s] the feed rate of reactant,  $M_m$  [g/mol] the atomic weight of depositing metal,  $A$  [cm<sup>2</sup>] the heated area over which deposition takes place, and  $\rho$  [g/cm<sup>3</sup>] the density of depositing metal.

This equation suggests that the deposition rate will decrease as the area  $A$ , over which deposition occurs, is increased, as long as all other parameters remain constant. This is a problem in hot-wall reactors where a large surface area exists that is heated to the same temperature as the substrate and is one reason why cold-wall reactors usually provide much higher deposition rates than hot-wall reactors. A key feature is that the deposition rate does not depend on the substrate temperature in this operating regime, as long as all other parameters remain constant. The (potential) rate of the surface reaction is much higher than the rate at which precursor is delivered to the reactor. As a result, the delivery rate limits the overall deposition rate.

Numerous examples of feed-rate-limited deposition are found in the literature. Feed-rate-limited deposition has been reported for LCVD of Au using Me<sub>2</sub>Au(hfac)<sup>[300]</sup> and for UHV CVD of Au from RAuPMe<sub>3</sub>.<sup>[289]</sup> It has also been reported for CVD of Cu from (hfac)CuL.<sup>[121, 127, 135]</sup> In most other cases (except for primarily Ni, W, Al and Mo) insufficient data have been reported to determine the mode of reactor operation.

### 5.2. Diffusion- and Surface-Reaction-Limited CVD

The overall deposition rate may be limited by the rate of the surface reaction if the feed rate is sufficiently high that it does not limit the deposition rate and diffusion (transport) limitations do not occur. This situation is obtained with high precursor throughputs at low pressures and low substrate temperatures with small substrate areas. At high pressures and temperatures corresponding to high reaction rates and slow transport of the reactant to the surface, transport-limited (diffusion-limited) deposition can occur (Figs. 3 and 4).

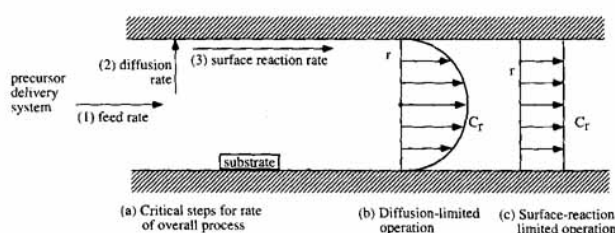


Fig. 3. Critical states for deposition which may limit the overall rate. a) Deposition rate determined by three steps in series, the slowest of which limits the overall rate. b) For diffusion-limited operation a concentration ( $C_r$ ) gradient exists for the reactant in the radial direction  $r$ . c) For surface-reaction-limited operation, reactant concentration is uniform in the radial direction  $r$ .

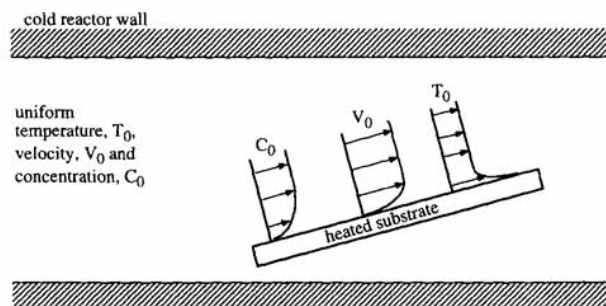


Fig. 4. Reactant concentration, velocity and temperature profiles for cold-wall reactor with inclined heated substrate.

The rate of deposition without limitations imposed by the feed-rate can be quantified.<sup>[299]</sup> The description below is not adequate to describe CVD processes quantitatively, but it describes the overall qualitative dependence of the rate on the relevant parameters. The analysis assumes a first-order surface reaction written in terms of the gas-phase concentration of the reactant at the surface. It also assumes diffusion through a concentration boundary layer of known thickness. The overall process consists of two steps in series: diffusion to the surface and surface reaction. The deposition rate is given by Equations 10–12.<sup>[299]</sup>

$$\text{rate} = \frac{C_r v_m}{1/k + L/D} \quad (10)$$

$$\text{rate} = k C_r v_m = k_0 [P_r/(RT)] v_m \exp[-E_A/(RT)] \text{ for } k \ll D/L \quad (11)$$

$$\text{rate} = \frac{v_m D C_r}{L} \quad (12)$$

$$= \left( \frac{v_m D_0}{L} \right) \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{P_r}{RT} \right) \text{ for } k \ll D/L$$

$$D = D_0 \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^{3/2} \quad (13)$$

Here  $D$  [ $\text{cm}^2/\text{s}$ ] is the diffusion coefficient,  $D_0$  [ $\text{cm}^2/\text{s}$ ] the diffusion coefficient at reference conditions,  $L$  [ $\text{cm}$ ] the thickness of the concentration boundary layer,  $k$  [ $\text{cm/s}$ ] the surface reaction rate constant,  $C_r$  [ $\text{molecules/cm}^3$ ] the reactant concentration outside the concentration boundary layer,  $C_s$  [ $\text{molecules/cm}^3$ ] reactant concentration immediately above substrate,  $k_0$  [ $\text{cm/s}$ ] pre-exponential constant,  $T_0$  [ $\text{K}$ ] the reference temperature for gas above the substrate,  $P$  [ $\text{dynes/cm}^2$ ] the total pressure,  $P_0$  [ $\text{dynes/cm}^2$ ] total pressure at reference conditions,  $P_r$  [ $\text{dynes/cm}^2$ ] reactant partial pressure outside the concentration boundary.

For large  $k$  ( $k \gg D/L$ ), the surface reaction is rapid and the rate is given by  $v_m D C_r / L$ , corresponding to a diffusion-limited process. This expression corresponds to the rate of diffusion of the reactant through the concentration boundary layer discussed above (see Fig. 4). For a slow reaction rate ( $k \ll D/L$ ) or rapid diffusion in the gas phase (large  $D$  or small  $L$ ), the rate is  $k C_r v_m$ , which is simply the rate of the surface reaction corresponding to surface-reaction-limited deposition.

Diffusion-limited LCVD of Au has been reported.<sup>[300, 301]</sup> Photochemical LCVD can also exhibit a diffusion-limited rate.<sup>[302]</sup> Examples of diffusion-limited CVD of Cu are also documented.<sup>[303]</sup> Similarly, diffusion-limited deposition of W, Al and Mo is common.

Precursor design influences the overall rate through the surface-reaction rate constant,  $k$ , and the reactant concentration,  $C_r$ , which can be no higher than the value corresponding to the vapor pressure. Reactor operating conditions influence the overall rate through  $D$  and  $L$ , which depend on a variety of parameters, including the temperature of the gas, the total pressure, carrier gas flow rate and properties, and reactor geometry.

### 5.3. Reactant Partial Pressure Dependence of Rate

In most cases, as the reactant concentration is increased the deposition rate increases as shown in Figure 5. For feed-rate-limited deposition, the rate does not depend on the precursor partial pressure or total pressure at a constant feed rate (Eq. 9). Therefore, increasing the total pressure while keeping the precursor feed rate constant has little effect on the rate. A test for this limit is to increase the feed rate while keeping all other parameters (total pressure, precursor partial pressure, temperature, etc.) constant and at the same time avoiding diffusion-limited deposition

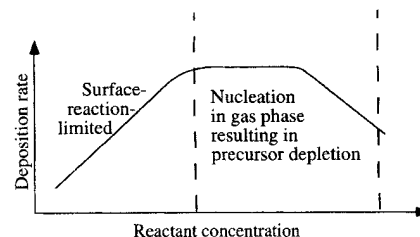


Fig. 5. Possible dependence of deposition rate on reactant concentration with gas-phase particle formation occurs.

(which can be influenced by changes in gas-flow rate). If the deposition rate increases, then the feed rate is the limiting factor.

For the case of diffusion-limited deposition, the rate is first order in reactant concentration, as shown by Equation 12 above. Doubling the pressure of the precursor doubles the rate of the reaction. This effect is sometimes mistakenly interpreted as a surface-reaction rate dependence on the precursor partial pressure to the first power (Eq. 11). A first-order dependence can be observed for diffusion-limited deposition regardless of the pressure dependence of the surface reaction as long as the surface reaction is sufficiently rapid. An indicator of diffusion-limited deposition is that increasing the total pressure while keeping the partial pressure of the precursor constant decreases the rate because the diffusion coefficient is inversely proportional to the total pressure  $P$ . Another test for diffusion-limited deposition is to vary the gas flow rate while keeping reactant concentration constant ( $C_r$  or  $P_r$ ). Varying the flow rate can result in variations in  $L$ , the thickness of the concentration boundary layer, which leads to changes in the deposition rate. Yet another test is to vary the carrier gas (He,  $\text{N}_2$ , Ar), while keeping other conditions fixed (see Eq. 12),<sup>[304]</sup> which varies the diffusion coefficient  $D$  through the influence on  $D_0$ . However, one of the best and most conclusive tests is to vary the substrate temperature as discussed below.

The case of surface-reaction-limited deposition is the only case for which the kinetics of the surface reaction can be observed (Eq. 12). The details of the surface reaction then determine the precursor-pressure dependence of the rate, which can be first order in some cases or can be more complex than the first-order reaction used here as an example. For example, deposition of Cu from  $(\text{hfac})\text{Cu}(\text{VTMS})$  exhibits a pressure dependence which varies as a function of temperature and precursor partial pressure.<sup>[127]</sup> The rate of tungsten deposition from  $\text{WF}_6$  also has a complex pressure dependence and can even be negative order in  $\text{WF}_6$  partial pressure.<sup>[305]</sup> Because a first-order dependence on precursor partial pressure can be observed for both surface-reaction-limited and diffusion-limited deposition, the best test for surface-reaction-limited deposition is to vary the substrate temperature and look for an exponential dependence of the deposition rate on the temperature.

### 5.4. Temperature Dependence of Rate

Feed-rate-limited deposition usually provides a rate with a weak temperature dependence. Increasing the surface temperature does not result in an increase in the rate, which can be no faster than the rate of delivery of the precursor into the reactor.<sup>[127, 289]</sup> A positive or negative order dependence of the rate on temperature can also occur if the reaction occurs in a hot-wall reactor and deposition occurs on the walls. In this case, increasing the temperature can result in deposition closer to the reactor inlet. Depending on the location of the substrate, this change may result in more deposition on the substrate if the region of highest deposition rate moves closer to the substrate or less deposition if this region moves away from the substrate.

For diffusion-limited deposition, the rate depends only weakly on the temperature primarily through the temperature dependence of the diffusion coefficient (see Eq. 12 above) which is roughly  $T^{3/2}$ .<sup>[304]</sup> This dependence<sup>[128]</sup> is far weaker than the exponential dependence of rate on temperature observed for surface-reaction-limited deposition and is nearly flat when plotted on a logarithmic scale. In addition, for diffusion-limited deposition, the precursor concentration at the surface is nearly zero and is not the same as the measured precursor partial pressure. This occurs because the potential rate of the surface reaction is rapid relative to the rate of transport to the surface.

Surface-reaction-limited deposition has a temperature dependence that varies with the details of the surface reaction. The deposition rate often increases as the substrate temperature is increased at low temperatures and low reactant concentrations, as shown in Figure 6. Because the rates of surface reactions are generally higher than those of

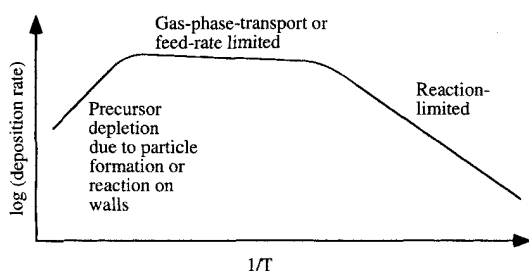


Fig. 6. Dependence of deposition rate on temperature.

homogeneous reactions, the slope of the line at low temperatures is usually related to the kinetics of the heterogeneous reactions, but in some cases may be related to homogeneous reaction kinetics. In the surface-reaction-limited regime, it is possible to measure the kinetics of the surface reaction and a rate increase as a function of temperature according to the Arrhenius relationship (Eq. 11). Also, the reactant concentrations at the substrate surface are often known because they are the same as the overall concentrations in the reactor if precursor conversion is low (Fig. 3). However, reactant

concentrations can be difficult to measure if the precursor has a low vapor pressure and a carrier gas is used.

Finally, as the substrate temperature is increased, gas-phase particle formation may occur, which depletes the reactant concentration in the gas phase and reduces the rate.<sup>[306]</sup> Alternatively, the reduction in the rate may be due to a thermodynamic limitation on reactant conversion or the rapid desorption of the precursor from the surface before reaction can occur. This behavior leads to the classical plateau in the deposition rate as a function of temperature, as shown in Figure 6.

## 6. Summary and Conclusions

We have summarized some general aspects of the CVD of metals. In spite of the large amount of work on CVD of metals, the behavior of many simple precursors has not been examined in detail. Even in the case of what appear to be simple precursors, the surface chemistry can be extremely complicated and difficult to interpret unambiguously. The CVD of W, Al, and Cu is the most studied; that of Mo, Pt, Pd, Ni, Ag, Rh, Ir and Au has been studied to a lesser extent. Most of the other metals have only been studied superficially. Several major conclusions can be drawn from the literature available on CVD of metals.

**Precursor Design.** Metal-containing precursors for the CVD of metal films must be volatile, low molecular weight species that contain substituents that can be completely eliminated during the surface reaction. It is difficult to provide specific precursor design rules for particular metals because there is a strong influence of the reactor geometry, deposition conditions and substrate interactions. It is clear that precursor design must be carefully matched to a given set of deposition conditions to achieve high-purity films.

The most commonly used precursors are metal halides, alkyls, carbonyls, cyclopentadienyls, and  $\beta$ -diketonates, but these are only suitable for some metals. Good precursors are available for CVD of W, Al, Cu, Mo, Rh, Pt, Pd, Ni, Ag, and Au. Many other metals do not have precursors which allow low-temperature deposition of high-purity films at high rates. This is true for Ti, which is important in the microelectronics industry.

More research is necessary in the area of precursor synthesis and characterization, including quantitative measurements of vapor pressures to allow estimates of transport rates. Improved methods of precursor delivery are necessary to enable the use of low-vapor-pressure precursors and to deliver precursors to substrates under controlled, reproducible conditions. Liquid delivery systems are promising in this regard and have been described elsewhere.

**Surface Chemistry.** Surface reaction mechanisms and reaction products are only known in a few cases, primarily for precursors to W, Cu, Au and Al films. The measurements of the surface reaction kinetics made for most systems are very limited, and the apparent activation energies for surface re-

actions are known for only a few precursors and surface compositions. Further work is needed to understand the reaction chemistry involved, which may lead to better strategies for blanket and selective CVD. This aspect is addressed in more detail under a discussion of selective CVD in Part 2.

**Reactor Design and Operation.** Better reporting and characterization of deposition conditions and substrate pretreatment are necessary to compare reports of blanket and selective CVD from different groups of investigators. Quantification of reactor by-product distributions from hot-wall CVD reactors and kinetic data from cold- or warm-wall CVD reactors is necessary. Insufficient information is given in most cases to determine the mode of reactor operation, i.e., surface-reaction-limited, feed-rate-limited, or transport-limited.

**Film Characterization.** The CVD of high-purity films of a variety of metals has been reported. Deposition rate, thickness, resistivity, and morphology are simple to determine and should be reported even when film purity cannot be determined for lack of equipment. In many cases it is not possible to evaluate the success of the CVD study because the resulting films are poorly characterized.

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