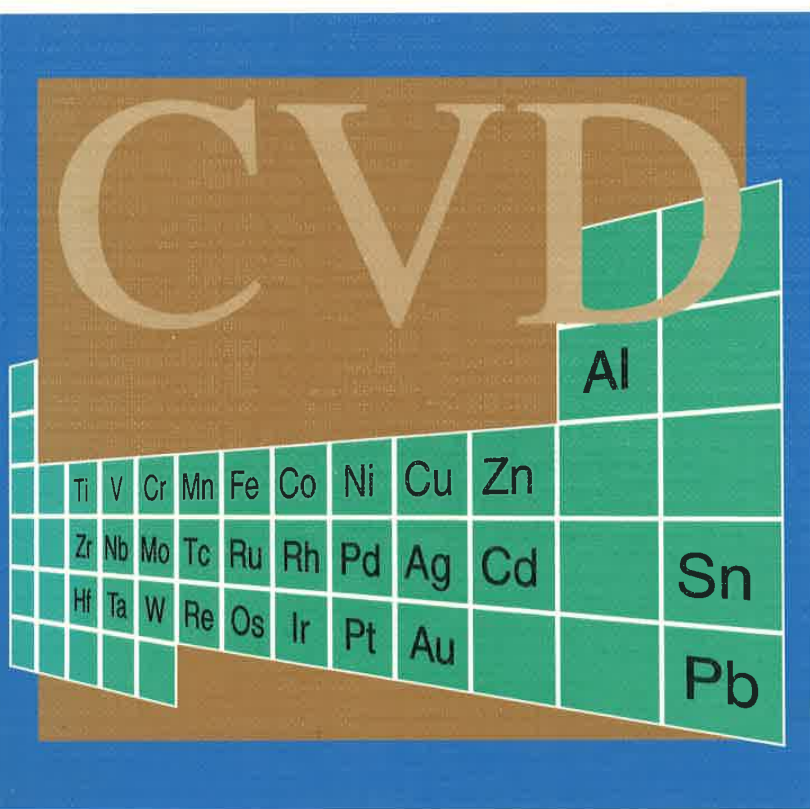


T. Kodas, M. Hampden-Smith

# The Chemistry of Metal CVD



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Toivo T. Kodas and Mark J. Hampden-Smith



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# **Chapter 8**

## **Chemical Vapor Deposition of Assorted Metals**

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### **Abstract**

The CVD of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Zn, Cd, Sn, and Pb is discussed. Precursors are grouped as metal-halide, alkyl, alkene, alkyne, allyl, cyclopentadienyl, arene, carbonyl, phosphine,  $\beta$ -diketonate, and alkoxide complexes for discussions of their characteristics, reaction mechanisms, and kinetics. In most cases, these metals have been studied to a limited extent, with the most comprehensive results being available for Nb, Ta, Cr, Mo, Fe, Ru, Co, Rh, and Ir. The precursors most extensively studied are metal halides, cyclopentadienyls, and carbonyls. Much less attention has been paid to developing organometallic precursors for deposition of high-purity films at low temperatures and high rates. Selective CVD has been studied for Mo but rarely for other systems.

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

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## 8.1 Introduction

In this Chapter we review the chemical vapor deposition (CVD) of several metals used for electronics and other applications. We include metals of Groups 4-9, 12, and the remaining elements of Group 14 (Sn, Pb) which are illustrated schematically in Figure 8-1. Not relevant to the present discussion include Group 1 alkali metal ions, which are extremely detrimental to the performance of electronic devices,<sup>1</sup> Group 2 alkaline earth, and Group 3 metals, all of which are seldom deposited by themselves. Also outside the scope of this discussion are metals used to form "13-15" or "III-V" materials,<sup>2-5</sup> the remaining metals of Groups 13 and 15, silicon, and germanium which have been reviewed in numerous articles and books elsewhere.<sup>6-22</sup> Earlier chapters focused on the metals that have been studied more extensively.

Key

	Chapter 2
	Chapters 4, 5
	Chapter 7

	Chapter 3
	Chapter 6
	Chapter 8

H																			He
Li	Be																		
Na	Mg																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac	Unq	Unp	Unh	Uns													

Figure 8-1 Schematic representation of metals reviewed in this and other chapters.

The properties of the metals we discuss, together with the corresponding data for the metals described in the other chapters, are presented in Table 8-1. For microelectronics applications, the resistivity and work function are probably the most important physical properties of the metal. However, melting point is important for high-temperature applications. Other properties important for a variety of applications include density, thermal expansion coefficient, thermal conductivity, oxidation resistance, and corrosion resistance.

There are many applications for these metals (see Table 8-2), and they can be grouped almost entirely by their properties, i.e., corrosion and oxidation protection, dopants in semiconductors, and electronic applications where the metal is used in elemental form or as a metal nitride, silicide, or oxide. Most applications are found in electronics where the



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O	F	Ne
S	Cl	Ar
Se	Br	Kr
Te	I	Xe
Po	At	Rn

other chapters.

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metals we discuss are interesting because of their potential use as contact, gate electrode, diffusion barrier, or interconnect materials in integrated circuits and packaging applications (see Ch. 1). In microelectronics applications, the ability to deposit pure, continuous, dense films with near-bulk physical properties is a critical aspect of CVD, and this aspect will be addressed in the following sections.

Table 8-1 Relevant Properties of Metals for Metallization Applications

Metal	Melting point (°C)	Resistivity ( $\mu\Omega\text{cm}$ )	Work Function (V)	Density ( $\text{g/cm}^3$ )
Al	660	2.65	4.08	2.7
Ti	1820	42.0	4.33	4.5
Zr	1750	40.0	4.21	6.5
Hf	2230	35.1	3.53	5.9
V	1915	25	4.30	6.1
Nb	2415	12.5	4.01	8.8
Ta	2996	12.5	4.19	16.6
Cr	1900	12.9	4.60	7.2
Mo	2625	5.2	4.20	10.2
W	3410	5.7	4.52 <sup>‡</sup>	19.3
Mn	1244	185.0	3.83	7.4
Re	3170	19.3	5.1	20
Fe	1535	9.71	4.04	7.9
Ru	2282	7.6 <sup>†</sup>	4.71	12.4
Os	3045	9.5	4.55	22.6
Co	1495	6.24	4.40	8.9
Rh	1960	4.51	4.8	12.4
Ir	2443	5.3	5.27	22.7
Ni	1455	6.84	5.02	8.2
Pd	1552	10.8	4.98	12.0
Pt	1769	10.6	5.34	21.4
Cu	1083	1.67	4.65	9.0
Ag	961	1.59	4.73	10.5
Au	1064	2.35	4.82	19.3

<sup>‡</sup> (001) face

<sup>†</sup> at 0 °C

Table 8-2 Applications of Metals

Ti	Adhesion layers, metal foils, corrosion resistant coatings, titanium aluminides, contacts in ICs, Ti:LiNbO <sub>3</sub> waveguides, TiN diffusion barriers, TiSi <sub>2</sub> contact layers
V	V-Si diodes, nitride diffusion barriers
Nb	Nuclear fuel particle coating, cladding for metal tubes, component of Nb <sub>3</sub> Ge and Nb <sub>3</sub> Ga superconductors, NbN diffusion barriers, metal alloy diffusion barriers, metal silicide contact layers
Ta	Capacitors, resistors, corrosion-resistant coatings, TaN and Ta-Si-N diffusion barriers, tantalum silicide contact layers
Cr	Corrosion protection, oxidation protection, possible contact metallization, CrN diffusion barriers, silicide contact layers
Mo	IC contact and gate metallization, MoSi <sub>2</sub> for microelectronics, Schottky contact metallization, wear resistant coatings, infrared reflector, laser mirror coating
Re	Heaters for furnaces, free standing shapes, contact layers, diffusion barriers, thermocouples, W:Re alloys
Fe	GaAs devices, FeN diffusion barriers, metal alloy and metal silicide diffusion barriers
Ru	Electrical contacts, diffusion barriers
Os	Thermionic diodes
Co	CoSi <sub>2</sub> for microelectronics, catalyst for electroless plating, possible interconnect in specialized applications
Rh	Electrical contacts, diffusion barriers
Ir	Corrosion protection, oxidation protection, thermionic cathodes, silicide diffusion barriers
Zn	Dopant in GaAs materials
Cd	Photoresist and mask repair
Sn	Dopant in GaAs and other materials, metal nitride diffusion barriers
Pb	Solder

Certain criteria can be established for the use of metals as conductors in integrated circuits, packaging applications, adhesion layers, and circuit boards. The metal films should have low resistivity, high melting points, be easy to etch, be stable in oxidizing environments, and at the same time be capable of oxidation. They should also have good mechanical stability, good adhesion characteristics, low stress, be stable to other processing steps, not contaminate devices, and not react with other materials. Unfortunately, most metals do not satisfy all or even many of these requirements as

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diffusion barriers,

nponent of Nb<sub>3</sub>Ge  
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l Ta-Si-N diffusion

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indicated in previous chapters. For example, while silver has the lowest resistivity of all metals, it is unstable on most surfaces with respect to oxidation, adhesion, and diffusion (see Ch. 6). Copper has low resistivity but a high diffusion rate into Si and SiO<sub>2</sub> necessitating the use of diffusion barrier layers if it is to be used in interconnect applications (see Ch.s 1, 4, and 5). Copper, like a number of noble metals, is also difficult to etch. Gold has low resistivity but forms a low melting (370 °C) alloy with silicon (see Ch. 6). For this reason, copper and gold are used in packaging applications where contact with silicon is not necessary.<sup>21</sup> With existing metallization schemes, aluminum is the metal with which industry has the most experience and which satisfies most of the requirements for integrated circuits (see Ch.s 1 and 2). The major drawbacks of aluminum, however, include its low electromigration resistance which limits critical current densities and its low melting point which is circumvented by deposition towards the end of the metallization scheme after the highest temperature step. Most of the other metals have resistivities which are too high for metallization applications but have certain unique combinations of properties that make them useful for other applications or make them attractive as components of other materials such as metal nitrides, silicides, and oxides.

A number of properties of metals have been identified that make them undesirable as conductors for very-large-scale integration (VLSI) and ultra-large-scale integration (ULSI) applications (Table 8-3). Many metals suffer from poor thermal or chemical stability, and this has inspired investigations of alloy materials which have significantly improved properties when compared to the individual elements. Molybdenum disilicide, MoSi<sub>2</sub>, is a classic example, and according to Galasso, it exhibits good electrical conductivity (100 μΩcm), has a high melting point, and is stable against chemical attack and oxidation even at elevated temperatures; cobalt disilicide, CoSi<sub>2</sub>, is another example.<sup>22</sup> The CVD of silicides, borides, and nitrides has been discussed in detail elsewhere.<sup>22</sup>

Purity levels of metals and other materials containing metal atoms may be impaired by several species used in electronics applications. In particular, the presence of alkali metal ions, generally sodium and potassium and radioactive isotopes, cause problems. Alkali metal ions present in the gate insulator are mobile and migrate to the silicon-insulator interface under the influence of an electric field; carrier mobilities are then diminished and the devices are then also unreliable.<sup>23</sup> The source of these impurities, apart from mishandling, is generally metals and reagents used in the fabrication process. The purity of sputtering targets is a concern for physically deposited films; the choice of reagents and the precursor purification processes are also important for CVD-derived metal films. Radioactive isotopes, particularly alpha-particle emitters such as uranium and thorium, are undesirable because they can lead to soft errors such as the accidental switching of transistors. Although there are no current specifications for tolerable levels of impurities, it is desirable to keep their concentration in the low ppb range.

Table 8-3 Undesirable Properties of Metals for Metallization Applications

Undesirable Property	Metal
Low melting point	Al Mg
Low eutectic temperature ( $<800^{\circ}\text{C}$ )	Au Pd Al Mg
Medium eutectic temperature ( $800^{\circ}\text{C} - 1100^{\circ}\text{C}$ )	Ni Pt Ag Cu
High diffusivity into Si	all
Interaction with $\text{SiO}_2$	Hf Zr Ti Ta Nb V Mg Al
High oxidation rate or poor oxidation stability	Refractory metals Rare earth metals Mg Fe Cu Ag
Poor chemical stability (especially in etching solutions)	Refractory metals Fe Co Ni Cu Mg Al
Poor etchability (i.e. good chemical stability)	Pt Pd Ni Co Au Cu
Poor electromigration resistance	Al

Some metals, other than those discussed in Chapters 2 through 7, may function quite well in future generations of integrated circuits. Where short distances are involved (e.g., first level metallization) higher resistivities can be tolerated. In these devices, the formation of patterned metal films will be necessary, and CVD is likely to remain an attractive method for metal-film deposition due to low deposition temperatures, conformal coverage, high purity, lack of radiation damage, and the possibility that selective deposition may be achieved.<sup>24</sup> The development of etching processes to achieve selective and anisotropic etching is also important. For example, Mo is a suitable metallization material because it has relatively low resistivity, is inert, has high-temperature stability, has a low thermal expansion coefficient, and can be etched.<sup>25</sup>

These properties make Mo suitable for incorporation into metallization schemes using existing fabrication techniques.

Other than for use as conductors, there are many applications of these metals for which CVD processes are suitable and a number of cases for which they have been used (Table 8-2). Titanium has been used extensively as an adhesion layer between a metal contact such as Pt and a metal oxide surface such as  $\text{SiO}_2$ .<sup>26</sup> It is also used as an adhesion layer between metal oxides and metals in packaging applications. Many metals have been deposited on reactive substrates to impart corrosion or oxidation resistance. Metals which have good corrosion resistance include Cr, Mo, W, Nb, Ta, and Ti.<sup>27</sup> Many metals are hard and are used as abrasion resistant coatings. For example, Rh has a higher melting point and is harder than Cu or Au. The noble metals tend to be inert with respect to oxidation.<sup>24</sup>

A number of metals have been deposited on substrates with the intention of inducing reactions with the substrate to form new phases which have specific beneficial properties. Applications of this approach exist for both the coatings and the microelectronics industries. For example, the deposition of Nb,<sup>28</sup> Zr, Ir and Mo<sup>29</sup> onto graphite substrates at high temperatures via CVD routes often results in formation of metal carbides and generally improves the high-temperature oxidation resistance of the substrate. Many metals, including Mo, Co,<sup>30-32</sup> and Ti,<sup>33</sup> when deposited on bare silicon substrates form metal disilicides at elevated temperatures. Laser CVD routes have also been used to deposit nuclei of various metals for subsequent electroless deposition processes.<sup>34</sup>

Many metal films have desirable optical properties. For example, Mo films have high infrared (IR) reflectivity (~97%) and are used in mirrors and other optical applications. In some cases, CVD methods produce films superior to those deposited by more conventional methods (e.g., Rh, electrochemically). In addition, metal nitrides and oxides incorporating metals have useful optoelectronic properties.

A number of metals exhibit properties that result in unique applications. For example, ruthenium films are mechanically strong and chemically inert and can exhibit oxidation resistance at temperatures up to 900 °C.<sup>35</sup> However, in the event of adventitious oxidation,  $\text{RuO}_2$ , the most stable oxide formed, exhibits a resistivity close to that of the metal and is generally not detrimental to the process. For this reason ruthenium may be applied as a contact material or diffusion barrier (see Ch. 1). Iron- and cobalt-containing films have been used for applications in high-speed, high-power semiconductor lasers due to their properties as semi-insulating confinement layers.<sup>36,37</sup> Iron-doped semi-insulating InP layers formed by the CVD of Fe, sometimes epitaxially, onto InP substrates have high resistivity and act as blocking layers in long wavelength lasers.<sup>36</sup> Rhenium forms high-strength alloys with tungsten and osmium, has a high melting point (3,000 °C), is exceptionally hard, and has a large work function.<sup>24</sup> Applications include high-temperature abrasion resistant coatings.

There are many studies of the catalytic behavior of these metals,<sup>38</sup> and in many cases, this interest has brought about a need to understand the interaction of metal-organic

molecules with metal surfaces.<sup>39,40</sup> Molecular information and mechanistic understanding is necessary for insight into ligand-design criteria for metal-organic CVD precursors. There is also extensive interest in the preparation of small metal particles by various techniques, including vapor-phase routes using volatile metal-organic precursors.<sup>41</sup> This interest is often driven by the desire to understand quantum confinement effects in these materials;<sup>42-44</sup> many physical and chemical properties such as electrical conductivity, optical properties, mechanical strength, melting point, catalytic reactivity and catalytic selectivity are size-dependent in the range 1-100 nm.<sup>45,46</sup> Chemical vapor deposition makes it possible to create thin films and fine particles with dimensions in this range. Furthermore, CVD offers the opportunity to co-deposit more than one metal, either from individual precursors or from a single multimetallic molecule, to prepare alloy films.<sup>47,48</sup> The reasons for developing CVD methods for the formation of metal films are addressed in Chapters 1 and 9.

It is important to pursue CVD routes as opposed to PVD (physical vapor deposition) or liquid-phase routes to attain conformal coverage, minimize interfacial reactions, avoid changes in stoichiometry during deposition, and reduce dopant redistribution and defects. It will become apparent in subsequent sections that there are many opportunities for the rational design of precursor molecules used to prepare films of these metals. In some cases, existing species are suitable as for  $\text{Fe}(\text{CO})_5$ ; however, only in a few examples have the precursors been designed specifically for the deposition of pure films. The greatest problem, again, is to develop precursors that will deposit high-purity material at low temperatures and high rates for thermally sensitive substrates.

In the following sections we will discuss the physical properties and structures of precursors. The CVD of these metals is summarized to include deposition parameters, kinetic data, selectivity where known, and physical properties of the films deposited. This is followed by a discussion of the kinetics and mechanisms of metal deposition from the different classes of precursors. Many precursors are photo-labile, especially metal carbonyls. Photochemically induced deposition of these metals, particularly using lasers, has been reviewed elsewhere<sup>34,49-51</sup> and is not discussed here. The CVD of other metals, Be,<sup>52</sup> U,<sup>53</sup> Pu,<sup>53</sup> B,<sup>54,55</sup> and Th<sup>56</sup> not discussed here, has been covered briefly in the literature.

## 8.2 Chemical and Physical Properties

### 8.2.1 Introduction

The following sections are organized according to the position of the metal in the Periodic Table (see Fig. 8-1). The metal-organic derivatives that have been used for CVD are shown in Tables 8-4 and 8-5 and are discussed below. The order of discussion is halides, followed by compounds with metal-carbon bonds, M-R where R = alkyl or aryl, metal-carbon  $\pi$ -complexes such as allyls, cyclopentadienyls and other arene complexes, metal carbonyls, metal trifluorophosphines, and derivatives with M-O bonds, e.g.,  $\beta$ -diketonates and alkoxides. Representative examples of the structures of each type of precursor are provided in most sections. These figures are intended to give the reader an appreciation of the metal coordination environment and ligand-bonding mode. These data are generally based on single-crystal X-ray diffraction structures obtained in the solid state and may not be an accurate representation of the structure in the gas phase. In general, there is a paucity of gas-phase structural information for CVD precursors.

Table 8-4 Precursors Used for Deposition of Various Metals

Metal	Derivative	Commercial Availability
Ti	TiI <sub>4</sub> , TiBr <sub>4</sub> , ( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	Yes
	"Ti( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	No
Zr	ZrI <sub>4</sub> , ZrBr <sub>4</sub>	Yes
	Zr(CH <sub>2</sub> - <i>t</i> -Bu) <sub>4</sub>	No
Hf	HfI <sub>4</sub>	Yes
V	VI <sub>2</sub> , VCl <sub>4</sub> , ( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )V(CO) <sub>4</sub>	Yes
Nb	NbCl <sub>5</sub> , NbBr <sub>5</sub>	Yes
Ta	TaCl <sub>5</sub> , TaF <sub>5</sub> , Ta(CO) <sub>5</sub>	Yes
Cr	CrF <sub>2</sub> , CrCl <sub>2</sub> , Cr(CO) <sub>6</sub> , [( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cr(CO) <sub>3</sub> ] <sub>2</sub>	Yes
	( $\eta^7$ -C <sub>7</sub> H <sub>8</sub> )Cr(CO) <sub>3</sub> , Cr( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	Yes
	Cr( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> - <i>i</i> -Pr) <sub>2</sub> , Cr(cumene) <sub>2</sub>	No
	Cr(CH <sub>2</sub> - <i>t</i> -Bu) <sub>4</sub> , Cr(N- <i>i</i> -Pr) <sub>3</sub>	No
Mo	MoF <sub>5</sub> , MoCl <sub>5</sub> , Mo(CO) <sub>6</sub>	Yes
	[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Mo(CO) <sub>3</sub> ] <sub>2</sub>	Yes

continued

Table 8-4 (continued)

Metal	Derivative	Commercial Availability
	$\text{Mo}(\eta^3\text{-allyl})_4$	No
Mn	$\text{Mn}_2(\text{CO})_{10}$	Yes
Re	$\text{ReF}_6$ , $\text{ReCl}_5$ , $\text{Re}_2(\text{CO})_{10}$ , $\text{ReOCl}_5$ , $\text{ReOCl}_4$	Yes
	$\text{HRe}(\text{CO})_5$	No
Fe	$\text{FeF}_3$ , $\text{Fe}(\text{CO})_5$ , $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	Yes
	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$	Yes
Ru	$\text{Ru}_3(\text{CO})_{12}$ , $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$ , $\text{Ru}(\text{acac})_2$	Yes
	$\text{Ru}(\text{hfb})(\text{CO})_4$	No
Os	$\text{OsCl}_4$	Yes
Co	$\text{CoCl}_2$ , $\text{Co}_2(\text{CO})_8$ , $\text{Co}_4(\text{CO})_{12}$	Yes
	$\text{Co}(\text{CO})_3(\text{NO})$ , $\text{HCo}(\text{CO})_4$	No
	$\text{CF}_3\text{Co}(\text{CO})_4$ , $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$	No
	$\text{Co}(\text{acac})_2$ , $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$	Yes
Rh	$\text{RhCl}_3$ , $\text{Rh}(\eta^3\text{-allyl})_3$ , $\text{Rh}(\text{tfac})_3$	Yes
	$[(\text{PF}_3)_2\text{RhCl}]_2$ , $(\text{acac})\text{Rh}(\text{CO})_2$	No
	$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ , $\text{Rh}(\eta^3\text{-allyl})(\text{CO})_2$	No
	$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$	No
	$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(1,5\text{-COD})$	No
	$(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$	No
Ir	$\text{IrF}_6$ , $\text{IrCl}_3$ , $\text{IrBr}_3$ , $\text{Ir}(\eta^3\text{-allyl})_3$	Yes
	$(\text{acac})\text{Ir}(1,5\text{-COD})$	Yes
	$\{[(\text{CH}_3)\text{O}]\text{Ir}(1,5\text{-COD})\}_2$ , $\text{Ir}(\text{acac})_3$	No
	$(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(1,5\text{-COD})$ , $(1,5\text{-COD})\text{Ir}(\mu\text{-OAc})_2$	No
	$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Ir}(1,5\text{-COD})$	No
Zn	$\text{Zn}(\text{CH}_3)_2$ , $\text{ZnEt}_2$	Yes
Cd	$\text{Cd}(\text{CH}_3)_2$ , $\text{CdEt}_2$	Yes
Sn	$\text{SnCl}_4$ , $\text{SnCl}_2$ , $\text{Sn}(\text{CH}_3)_4$ , $\text{SnEt}_4$	Yes
	$\text{Sn}(-n\text{-Bu})_4$ , $\text{Sn}(-n\text{-Bu})_2\text{Cl}_2$	Yes
Pb	$\text{PbEt}_4$ , $\text{PbPh}_4$	Yes

Source of data: Chem Sources - USA, Directors Publishing Company, Clemson, South Carolina 29633-1824, 1992.



Table 8-5 Heterometallic Precursors  
Used for Deposition of Various Metals\*

Metals	Derivative
Mn/Ge	$\text{CH}_2\text{CR}=\text{CRCH}_2\text{Ge}$ $[\text{Mn}(\text{CO})_5]_2$
Mn/Si	$\text{H}_3\text{SiMn}(\text{CO})_5$
Fe/Si	$(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$
Fe/Co	$(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$ $\text{HFeCo}_3(\text{CO})_{12}$ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_2\text{Co}(\text{CO})_9$
Fe/Ni	$(\eta^5\text{-C}_5\text{H}_5)_2\text{FeNi}(\text{CO})_3$
Co/Si	$(\text{H}_3\text{Si})\text{Co}(\text{CO})_4$
Co/Ga	$(\text{CO})_4\text{CoGaCl}_2(\text{THF})$
M/E	$\text{L}(\text{CO})_n\text{M-ER}^1\text{R}^2(\text{D})$ where $\text{L} = \text{CO}, (\eta^5\text{-C}_5\text{H}_5)$ $n = 1\text{-}4$ $\text{M} = \text{Mn, Fe, Co, Ni}$ $\text{E} = \text{Al, Ga, In}$ $\text{R} = \text{H, alkyl}$ $\text{D} = \text{O or N donor ligand.}$

\* Not commercially available

## 8.2.2 Precursor Characteristics

There are several rationales for the choice of ligands that have been used to satisfy the metal coordination environment and electroneutrality in CVD precursors. In many cases, commercial availability has been the major criterion. In fewer cases, the ligands have been chosen to provide suitable precursor deposition characteristics. Some comments on the suitability of the species identified in Tables 8-4 and 8-5 that have been used for CVD or, in many cases, the attempted CVD of metals are warranted. In most sections, a table is given to provide information about properties.

### 8.2.2.1 Metal Halides

Metal halides are generally unsuitable for CVD for three reasons: (i) generally, they do not thermally decompose below 500 °C, (ii) they can give halide-contaminated films,

and (iii) they often have low volatility (see also Ch. 3). The temperature of thermal decomposition and the purity of the film can be improved in many cases by the addition of a reducing agent during the deposition. Typical reducing agents include  $H_2$  and  $SiH_4$ . Changing to a halide substituent lower in Group 17 (e.g., Br or I as opposed to F or Cl) will tend to lower the thermal decomposition temperature due to a weakening of the M-X bond as a result of the lower electronegativity of the Group 17 element upon descending the group and the larger size of the halide relative to the size of M.<sup>57-60</sup> Table 8-6 gives some relevant properties of metal halides, most of which are available commercially.

Table 8-6 Properties of Selected Metal Halides

Halides	Melting Point °C	Boiling Point °C
$SiCl_4$	-70	58
$VCl_4$	-28	149
$TiCl_4$	-25	136
$MoF_6$	18	35
$ReF_6$	19	48
$MoCl_5$	194	268
$NbCl_5$	205	254
$TaCl_5$	216	242
$TaBr_5$	265	349
$HfCl_4$	319	319(s)
$ZrCl_4$	437	331(s)
$ZrBr_4$	450	357(s)
$HfI_4$	---	400(s)
$CrCl_2$	824	1300(s)

(s) = sublimes

Low volatility is a major problem because it makes transport of the precursor to the CVD reactor difficult and leads to low deposition rates (see Ch. 1). The reason for the general lack of volatility is that in many cases the preferred coordination number of the ion exceeds its oxidation state. This frequently results in oligomerization where the halide ligands bridge metal centers by using one or more of their available lone pairs. One solution to this problem is to use fluoride ligands, because, although they are small and might be expected to facilitate a higher coordination number at the metal center compared to other halides, they are less inclined to form bridges, and as a result, they impart volatility to the metal center. In addition, fluorine tends to stabilize higher

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oxidation state precursors better than other members of Group 17 due to its higher electronegativity. This is advantageous because it decreases the tendency for oligomerization by approaching the limit of coordination number = oxidation state which increases the vapor pressure.

A classic example is the case of  $WF_6$  where the coordination sphere of  $W^{VI}$  is satisfied by six fluoride ligands resulting in the formation of a highly volatile complex. The halides  $SnCl_4$  and  $TiCl_4$  are other examples where the metal coordination number and oxidation state are satisfied with the result that oligomerization is unnecessary and these species exist as volatile liquids at room temperature and pressure (Fig. 8-2).<sup>61</sup> (It should be noted, however, that higher coordination numbers for  $Sn^{IV}$  and  $Ti^{IV}$  are common.) In contrast,  $SnCl_2$  is an infinite polymer in the solid state because the number of ligands is lower than the preferred coordination number and makes  $SnCl_2$  unstable with respect to oligomerization (Fig. 8-2).<sup>62-64</sup> However,  $SnCl_2$  can be thermally de-oligomerized to form a monomeric species in the gas phase.<sup>65</sup> The drawback to this approach is that the use of complexes with a formally high oxidation state may require more forcing conditions (i.e., higher substrate temperature or presence of a reducing agent) to reduce the complex and to form the metal compared to lower oxidation state analogs.

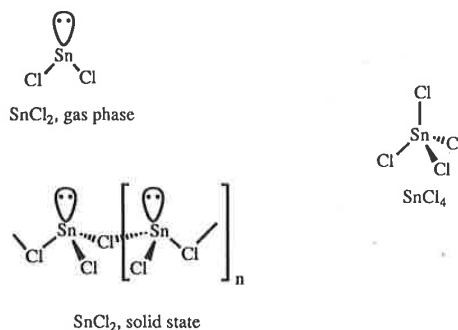


Figure 8-2 Structures of  $SnCl_4$  and  $SnCl_2$  illustrating relationship between preferred coordination number and oxidation state.

The halides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Re, Fe, Os, Co, Ir, and Sn have been used as precursors for CVD experiments at elevated temperatures where thermally sensitive substrates were not used and low substrate temperatures were not necessary.<sup>31,66-68</sup> A typical reaction is shown in Equation 8.1.



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### 8.2.2.2 Metal Alkyls

Similar trends in coordination number and oxidation state are broadly true for ligand environments other than halides. Where the coordination number of the metal is not satisfied, oligomerization generally occurs resulting in lowering of the volatility when compared to monomeric complexes. Homoleptic (possessing only one type of ligand) metal alkyl, and aryl derivatives of the transition elements are often thermally unstable at room temperature.<sup>57</sup> For example  $\text{W}(\text{CH}_3)_6$  is a volatile solid that is capable of detonation because the alkyl substituents are insufficiently electronegative to stabilize the high oxidation state (VI) of W. Table 8-7 gives some properties of metal alkyls. In general, most metal alkyls have low melting and boiling points and high vapor pressures. The primary reason they have not been used for CVD of many elements is that carbon-contaminated films are produced. Also, they are often pyrophoric, explode on contact with water, and are toxic.

Table 8-7 Properties of Selected Metal Alkyls

Compound	Formula	MP (°C)	BP (°C)	Vapor Pressure mm Hg
Diethyl beryllium	$(\text{C}_2\text{H}_5)_2\text{B}$	12	194	---
Dimethyl cadmium	$(\text{CH}_3)_2\text{Cd}$	4	105	28/20 °C
Tetraethyl tin	$(\text{C}_2\text{H}_5)_4\text{Sn}$	-112	181	---
Tetramethyl tin	$(\text{CH}_3)_4\text{Sn}$	-54	75	---
Dimethyl zinc	$(\text{CH}_3)_2\text{Zn}$	-42	46	124/0 °C
Diethyl zinc	$(\text{C}_2\text{H}_5)_2\text{Zn}$	-28	118	6.4/20 °C

Transition metal alkyl complexes have not been studied extensively as precursors for the CVD of metal films. In the absence of a reducing atmosphere such as  $\text{H}_2$ , metal carbides are normally formed as in the case of  $\text{Ti}(\text{CH}_2\text{-}t\text{-Bu})_4$ .<sup>69</sup> However, metal alkyl derivatives of the relevant main group metals, Sn and Pb, and the pseudo-main group metals,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  (both  $d^{10}$ ) have been used for metal deposition. This is probably because these derivatives exhibit sufficient thermal stability that they can be handled at room temperature, they are generally monomeric (see Fig. 8-3), exhibit suitable vapor pressures, and generally thermally decompose at elevated temperatures to liberate the corresponding metal. Some metal alkyl complexes contain bridging alkyl groups or agostic interactions which may be detrimental to their use as precursors for CVD of metals.<sup>70</sup>



Figure 8-3 Structure of typical metal alkyl precursors,  $\text{Zn}(\text{CH}_3)_2$  and  $\text{M}(\text{CH}_2-t\text{-Bu})_4$ ,  $\text{M} = \text{Ti, Zr}$ .

Thermal decomposition of metal alkyls to form pure metal may occur by any of three methods, (a)  $\beta$ -hydride elimination (well known in Al CVD; see Ch. 2), (b)  $\alpha$ -C-H abstraction, or (c) M-C bond homolysis (Fig. 8-4).<sup>70</sup> In many cases  $\beta$ -hydrogens are not present in the precursors (i.e., methyl derivatives) and preclude the  $\beta$ -hydride elimination mechanism. Metals at the lower end of a given group in the periodic table tend to have weaker M-C bonds, and as a result, are more likely to undergo M-C bond homolysis compared to those at the higher end. This is particularly the case for lead(IV) alkyl compounds. While some examples of volatile lower oxidation state alkyls of tin ( $\text{Sn}^{\text{II}}$ ) and lead ( $\text{Pb}^{\text{II}}$ ) are known,<sup>71</sup> they have not been used in CVD experiments.

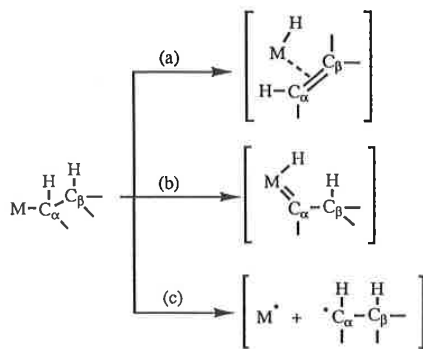


Figure 8-4 Diagrammatic representation of (a)  $\beta$ -hydride elimination, (b)  $\alpha$ -hydrogen-abstraction, and (c) M-C bond homolysis pathways which can occur on thermal decomposition of metal alkyl compounds.

### 8.2.2.3 Complexes with Unsaturated Organic Ligands: Alkenes, Alkynes, Allyls, $\eta^5$ -Cyclopentadienyls, $\eta^6$ -Arenes, and Related Complexes

This section includes discussion of derivatives such as olefin and alkyne complexes, metal allyls, complexes with aromatic cyclic ligands such as cyclopentadienyl or cycloheptatrienyl and metallocenes [i.e.,  $M(\eta^5\text{-C}_5\text{H}_5)_2$ , e.g., ferrocene], and arene complexes. Examples of each of these compounds are known for most transition elements. A number of metallocene and arene derivatives of the main group metals are known, but they are not common (due to their full underlying d-shells) and have not been reported as precursors for CVD experiments. A note of distinction is necessary to avoid confusion: Metallocene and other cyclopentadienyl or cycloheptatrienyl complexes and metal allyls contain  $\pi$ -bonded ligands which are negatively charged, whereas olefin, alkyne, and arene ligands are neutral (i.e.,  $\eta^6\text{-C}_6\text{H}_6$  ligands). Examples are  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$  in which the Cr is formally zero-valent and  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  where Fe is formally divalent.

**Alkene and Alkyne Adducts:** Alkene adducts of various transition metals have been used to deposit metal films. Depending on the nature of the metal center and its oxidation state, alkene adducts can exist in bonding modes that vary anywhere between the two extremes of  $M^{n+}(\text{CH}_2=\text{CH}_2)_n$  ( $\pi$ -bonded olefin) and  $M^{(n+2)+}(\text{CH}_2\text{-CH}_2)_n$  (metallacyclopropane), where alkene = ethylene as shown in Figure 8-5.<sup>70</sup> A similar situation holds for alkyne adducts. These different coordination modes are likely to significantly affect the strength of the metal-olefin and metal-alkyne bonds and change the CVD behavior of the precursor. Insufficient data are available to tabulate the properties of alkene and alkyne complexes that have been used as precursors for CVD by metals.

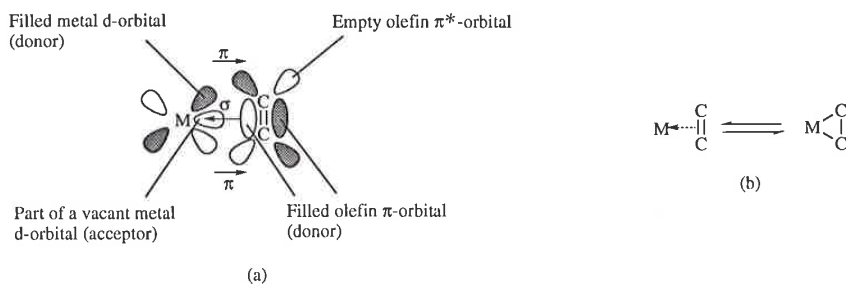
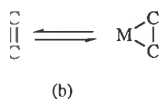


Figure 8-5 (a) Nature of orbital interaction between a transition metal and an alkene ligand. Arrows indicate direction of electron donation. (b) Two canonical form extremes result from extent of overlap between orbitals shown in (a).

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It is difficult to generalize about the suitability of such species as precursors for the deposition of pure metal films. However, olefin adducts of the noble metals are likely to be suitable because under a hydrogen atmosphere they are likely to catalyze hydrogenation of the olefin or alkyne rendering it less reactive and allowing it to cleanly desorb from the surface. Examples that have been studied include  $[(\text{CH}_3\text{O})\text{Ir}(1,5\text{-COD})]_2$ ,  $[(\text{AcO})\text{Ir}(1,5\text{-COD})]_2$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(1,5\text{-COD})_2$ , and  $\text{Ru}(\text{hfb})(\text{CO})_4$  and will be discussed in their appropriate sections. The structure of a typical olefin adduct that has been used in CVD experiments is shown in Figure 8-6.

**Metal Allyls:** Metal allyl (or propenyl) complexes are known for a variety of transition and main group elements, and a number of these derivatives have been used for CVD experiments. In general these species are less labile compared to alkyl compounds because the allyl ligand often acts as a four electron donor and can also act as a  $\pi$ -acceptor (assuming an  $\eta^3$ -coordination mode). These interactions strengthen the metal allyl bond compared to the metal alkyl bond. In addition the  $\eta^3$ -allyl ligand occupies two coordination sites at the metal center and as a result stable monomeric metal allyl complexes are formed where the oxidation state is less than the preferred coordination number. To continue the analogy with  $\text{W}(\text{CH}_3)_6$  above,  $\text{M}(\text{allyl})_4$ ,  $\text{M} = \text{Mo}$  and  $\text{W}$ , are monomeric complexes where oligomerization is prevented by the steric protection of the metal center afforded by the four allyl groups as shown in Figure 8-7.<sup>72,73</sup> Insufficient data are available to tabulate the properties of metal allyl compounds that have been used as precursors for CVD of metals.

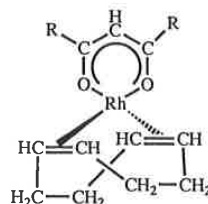


Figure 8-6 Structure of metal olefin adduct:  $(\text{hfac})\text{Rh}(1,5\text{-COD})$ .

Homoleptic allyl compounds of  $\text{Rh}$ ,<sup>74</sup>  $\text{Ir}$ ,<sup>74</sup>  $\text{Mo}$ ,<sup>75</sup>  $\text{W}$ ,<sup>75</sup> and  $\text{Pd}$ <sup>76</sup> have been studied as precursors in CVD experiments. The noble metals<sup>74,76</sup> give rise to films with relatively low carbon, whereas the more electropositive metals ( $\text{Mo}$ ,  $\text{W}$ ) result in formation of carbides and/or incorporation of graphitic carbon in the growing film.<sup>74</sup>

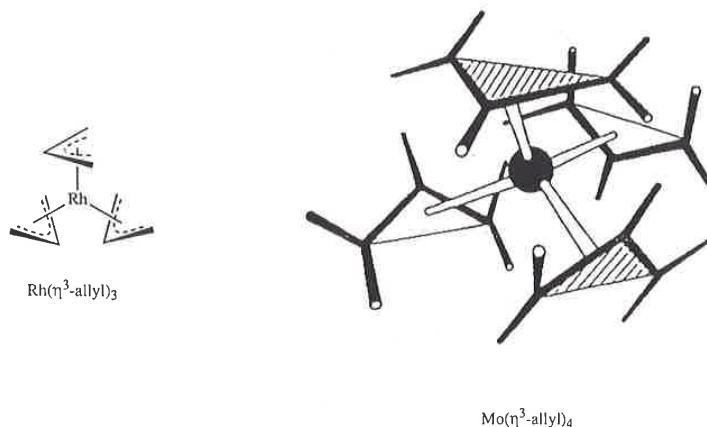


Figure 8-7 Structures of homolytic metal  $\eta^3$ -allyl complexes;  $\text{Rh}(\eta^3\text{-allyl})_2$  and proposed structure of  $\text{Mo}(\eta^3\text{-allyl})_4$ .

**$\eta^5$ -Cyclopentadienyl and Related Complexes:** Complexes containing cyclopentadienyl ligands generally exhibit higher stability compared to alkyl complexes because these ligands occupy more of the metal coordination sphere and form stronger bonds to the metal center. For example, ferrocene can be considered a six-coordinate complex of  $\text{Fe}^{\text{II}}$ , where each cyclopentadienyl ligand occupies three coordination sites at the metal center (see Fig. 8-8). This results in reasonable volatility for these complexes, but the lower lability of  $\pi$ -bonded ligands generally results in carbon incorporation into the final film, especially for the more electropositive metals. Ferrocene, for example, is unusually thermally stable and in the absence of  $\text{H}_2$  does not decompose below  $500^\circ\text{C}$ . Similar properties are expected for other  $\pi$ -bonded anionic ligands such as  $\eta^7$ -cycloheptatrienyl. Chemical vapor deposition using individual metallocene complexes of Fe, Ru, and Co has been studied. A number of other mixed-ligand cyclopentadienyl and cycloheptatrienyl carbonyl complexes, including  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ ,  $(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3$ , and  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ , have also been studied. As for the metallocene derivatives, the  $\pi$ -bonded ( $\eta^5\text{-C}_5\text{H}_5$ ) and ( $\eta^7\text{-C}_7\text{H}_7$ ) ligands are expected to be strongly bonded to these metal centers. For later transition elements, and those lower in a group, these bonds are likely to be weaker and clean removal of the ligand is more likely as for  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(1,5\text{-COD})$ , and  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Ir}(1,5\text{-COD})$  (see also Ch. 7).



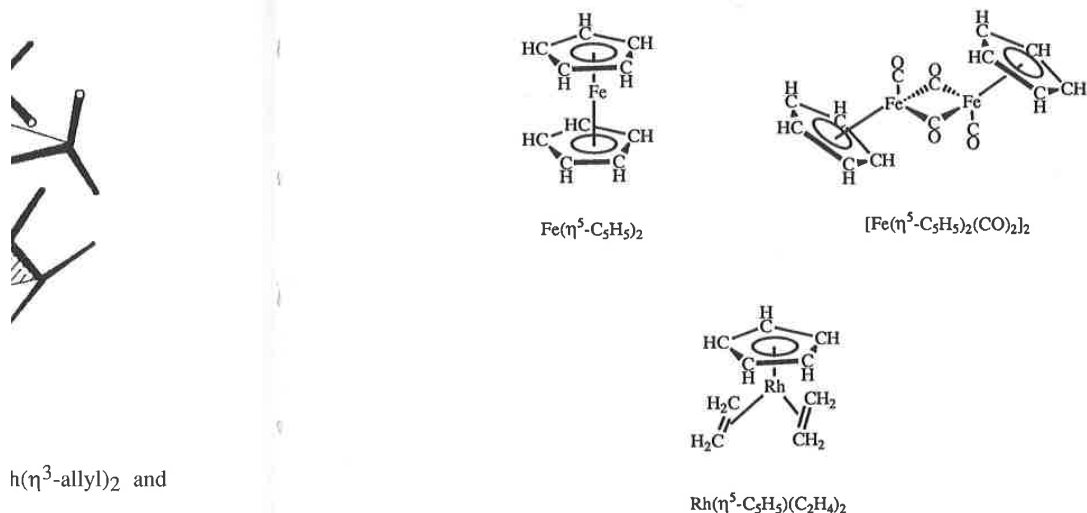


Figure 8-8 Structures of some  $\eta^5\text{-C}_5\text{H}_5$  complexes used for CVD,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2]_2$ , and  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$ .

**$\eta^6$ -Arene and Related Complexes:** Arene complexes are likely to suffer from similar problems as those expected for metallocene and related complexes. Arene ligands coordinated through more than one site, i.e., multihapto ligands, have a high enthalpic and entropic stability against ligand dissociation (see Fig. 8-9). Examples of the compounds that have been studied are  $\text{Cr}(\text{cumene})_2$  and  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ . Both gave metal carbides rather than chromium metal.<sup>77</sup> Insufficient data are available, however, to tabulate the properties of metal arene complexes that have been used as precursors for CVD of metals.

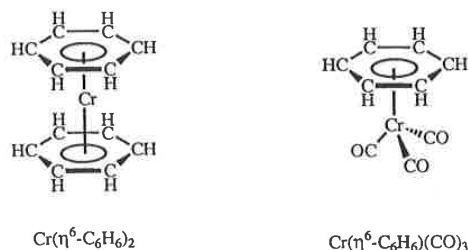


Figure 8-9 Structures of typical  $\eta^6$ -arene complexes.

#### 8.2.2.4 Metal Carbonyls

Metal carbonyls are commonly thermally stable at room temperature due to the well known  $\sigma$ -donor,  $\pi$ -acceptor bonding of this ligand (see Fig. 8-10).<sup>70</sup> Their properties are shown in Table 8-8. The results of a solid-state structural study of two archetypal mononuclear metal carbonyls are presented in Figure 8-11.<sup>78</sup> They are volatile in general but are not used for CVD of many materials because carbon- and oxygen-contaminated films frequently occur. In addition, many carbonyls such as those of Fe are toxic. Related compounds that are suitable for CVD are various substituted metal carbonyls including halides and nitrosyl species such as  $\text{Co}(\text{NO})(\text{CO})_3$ <sup>79</sup> (see also Ch. 7).

Table 8-8 Properties of Metal Carbonyls and Carbonyl Halides

Compound	MP °C	BP °C	Color / Form	Comments
<u>MONONUCLEAR</u>				
$\text{V}(\text{CO})_6$	65	dec.	Black crystal	Yellow-Orange in solution, volatile, very unstable
$\text{Cr}(\text{CO})_6$	164	dec. 180	White crystal	Volatile
$\text{Fe}(\text{CO})_5$	-20	103	Yellow liquid	Poisonous
$\text{Mo}(\text{CO})_6$	150	dec. 180	White crystal	Volatile
$\text{Ru}(\text{CO})_5$	-22	---	Colorless liquid	Very volatile
$\text{Os}(\text{CO})_5$	-15	---	Colorless liquid	Very volatile
<u>DINUCLEAR</u>				
$\text{Mn}_2(\text{CO})_{12}$	152	---	Yellow	---
$\text{Fe}_2(\text{CO})_9$	80	---	Yellow	Volatile
	dec.		crystal	
$\text{Co}_2(\text{CO})_8$	51	52	Orange	CO loss
		dec.	crystal	

continued

Table 8-8 Continued

Compound	MP °C	BP °C	Color / Form	Comments
Re <sub>2</sub> (CO) <sub>10</sub>	170	250 dec.	Colorless crystal	Volatile
Ir <sub>2</sub> (CO) <sub>8</sub>	160	---	Yellow crystal	Sublimes in CO at 160 °C
<b>CARBONYL HALIDES</b>				
Mn(CO) <sub>5</sub> Cl	---	---	Yellow	Loses CO at 120 °C in organic solvent
Re(CO) <sub>4</sub> Cl <sub>2</sub>	---	250 dec.	White crystal	---
Ru(CO) <sub>2</sub> I <sub>2</sub>	---	---	Orange powder	Suitable for CVD
Os(CO) <sub>3</sub> Cl <sub>2</sub>	270	280 dec.	Colorless prism	Suitable for CVD
[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	125 sub.	---	Ruby red needle crystal	Suitable for CVD
[Ir(CO) <sub>2</sub> Cl] <sub>2</sub>	140	---	Colorless needle crystal	Suitable for CVD

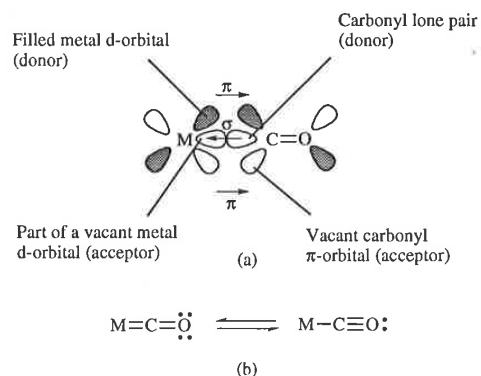


Figure 8-10 (a) Nature of orbital interaction between a transition metal and a carbonyl ligand. Arrows indicate direction of electron donation. (b) Two canonical form extremes result from extent of overlap between orbitals shown in (a).

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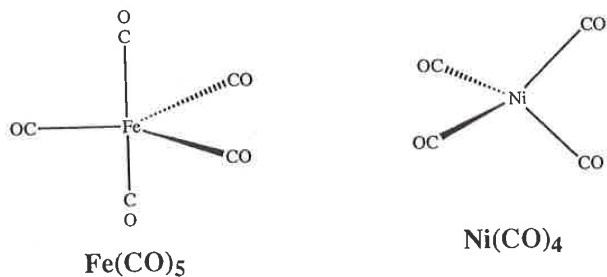


Figure 8-11 Structures of two homoleptic mononuclear metal carbonyl compounds,  $\text{Fe(CO)}_5$  and  $\text{Ni(CO)}_4$ .

Metal carbonyl derivatives of virtually all the transition elements are known and monomeric derivatives occur for  $\text{M(CO)}_6$  ( $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$ ),  $\text{Fe(CO)}_5$ , and  $\text{Ni(CO)}_4$ . Furthermore, the metal is formally in the zero valent oxidation state in a homoleptic metal-carbonyl compound which, in principle, should enable simple dissociation of carbon monoxide to liberate the element itself without the need for a reduction step.



Although many such equations for numerous metal carbonyls have been written for CVD reactions, this simple elimination reaction does not represent the whole picture. In the cases of Co, Fe, and Ni, high-purity deposits can be obtained. Nevertheless, films deposited from other metal carbonyl compounds [ $\text{Cr(CO)}_6$ , for example] are invariably contaminated with metal carbides, metal oxides, and graphitic carbon. This is not surprising when the canonical form  $\text{M}=\text{C}=\text{O}$  (Fig. 8-10) is considered,<sup>70</sup> and when it is noted that many of the metals being deposited can catalytically cleave the C-O bond of carbon monoxide (e.g., W) under the deposition conditions employed.<sup>80</sup>

Many examples of homopolynuclear and heteropolynuclear metal carbonyls exist and some of these species have been used for CVD experiments.<sup>30,81,82</sup>

#### 8.2.2.5 Metal Trifluorophosphines

In some respects, homoleptic metal trifluorophosphine derivatives are analogous to homoleptic metal carbonyl derivatives. The metal is in the zero-valent oxidation state and is coordinated to ligands that on cleavage of the metal-ligand bond release a highly volatile by-product. In principle, the trifluorophosphine derivatives should be more suitable as precursors for metal CVD compared to metal carbonyls since they are volatile,

the  $\text{PF}_3$  ligand is a poor  $\sigma$ -donor,  $\text{PF}_3$  itself is very volatile (b.p. =  $-101.8^\circ\text{C}$ ), and the  $\text{PF}_3$  ligand usually does not dissociate on the metal surface. The synthesis and properties of the trifluorophosphine complexes of Re, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir, and Pd are discussed by Kruck.<sup>83</sup> These complexes have decomposition temperatures of  $-20$  to  $300^\circ\text{C}$  and high vapor pressures. However,  $\text{PF}_3$  is known to react with Si substrates under some conditions to form P and liberate  $\text{SiF}_4$  (see Ch. 3) which makes these precursors undesirable for some electronics applications.

Complexes with  $\text{PF}_3$  have been used to deposit metal films at temperatures between  $200$  and  $300^\circ\text{C}$ . A patent discusses the use of metal trifluorophosphine and trifluorophosphine hydride complexes for CVD at temperatures of  $350$ – $600^\circ\text{C}$ .<sup>84</sup> However, CVD using these precursors has not been studied extensively.<sup>85–87</sup> In other cases, the metal is not zero valent and the complex contains other ligands along with  $\text{PF}_3$ . The structure of such a trifluorophosphine complex is shown in Figure 8-12.<sup>88</sup>

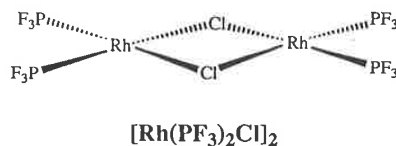


Figure 8-12 Structure of  $[(\text{PF}_3)_2\text{RhCl}]_2$ .

### 8.2.2.6 Metal $\beta$ -diketonates

As precursors for CVD experiments, metal  $\beta$ -diketonates, particularly the fluorinated derivatives, have the advantage that they generally exhibit high vapor pressures but have the disadvantages that they do not generally decompose below  $300^\circ\text{C}$  and that the deposit is often contaminated unless a reducing agent such as  $\text{H}_2$  is added (Eq. 8.3).



Metal  $\beta$ -diketonates (Table 8-9) show melting points well over  $100^\circ\text{C}$  and often near  $200^\circ\text{C}$ . All are solids at room temperature and have relatively high vapor pressures as discussed in Section 8.2.3 below. Several review articles and books discuss their synthesis and properties.<sup>89–99</sup> Graddon discusses Zn, Mn, Cu, Ni, Co, and Fe  $\beta$ -diketonate complexes.<sup>93</sup> Their volatility is enhanced because the  $\beta$ -diketonate ligand is bidentate when bonded through the oxygen ligands, although this is not always the case, and generally prefers to chelate rather than bridge. Examples of monomeric  $\beta$ -diketonate complexes can be found in Chapters 4, 5, 6, and 7. To emphasize the possibility of oligomerization, examples of oligomeric, homoleptic metal  $\beta$ -diketonate compounds are

shown in Figure 8-13. In some cases, extra coordination sites have been consumed by coordination of a Lewis base such as in the case of  $(\beta\text{-diketonate})\text{CuL}_n$  compounds, described in Chapter 5, which prevents oligomerization. In other cases (e.g., Ni, Co), the  $\beta\text{-diketonate}$  is forced to bridge as well as chelate resulting in complex structures (see Fig. 8-13).

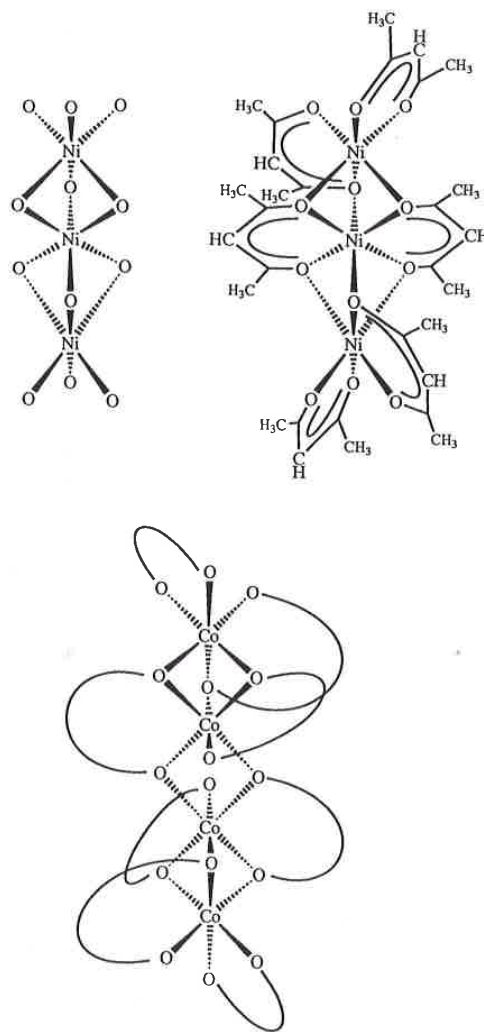


Figure 8-13 Examples of typical homoleptic metal  $\beta\text{-diketonate}$  compounds:  $[\text{Co}(\text{acac})_2]_4$  and  $[\text{Ni}(\text{acac})_2]_3$ .

Table 8-9 Properties of Selected Metal  $\beta$ -Diketonates

Metal	Formula	Form	Melting Point °C
Chromium	$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$	Violet crystal	214
Cobalt	$\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$	Green crystal	240
Iron	$\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$	Orange crystal	179
Lead	$\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$	White crystal	---
Manganese	$\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2$	Buff crystal	180
Rhodium	$\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)_3$	Yellow crystal	---
Zinc	$\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$	White needles	138
Zirconium	$\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$	White crystal	172

A number of mixed ligand  $\beta$ -diketonate complexes of noble metals including  $\text{Rh}(\text{CO})_2(\text{acac})$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{acac})$  have been used for CVD experiments.<sup>100-105</sup>

### 8.2.2.7 Metal Alkoxides

Some metal alkoxide compounds are volatile where the alkoxide ligand is sterically demanding, but they are generally not suitable as precursors for deposition of metals {see Ch. 5,  $[\text{Cu}(\text{O}-i\text{-Bu})_4]$ . In most cases metal oxides are deposited, especially when the metal center is electropositive, as in Ti.<sup>106</sup> Occasionally, films of transition metals such as Cu have been deposited from these precursors.<sup>107</sup>

### 8.2.3 Vapor Pressures

Since volatility is only one of the criteria used to select a metal-organic compound for use as a CVD precursor, extensive discussion of these data are not warranted. However, vapor pressure data demonstrate the temperature range over which the precursors are stable as well as the temperature to which they must be heated to carry out CVD. As a rule of thumb, a vapor pressure of at least 100 mtorr is essential for a metal-organic compound to give a sufficiently high deposition rate for most applications using conventional precursor delivery methods. This criterion excludes many potential precursors because they thermally decompose before a sufficiently high vapor pressure is reached.

For comparison, vapor pressure data for representative examples of classes of precursors are presented in Figure 8-14 and Table 8-10. The compounds  $\text{WF}_6$  and  $\text{MoF}_6$  exhibit relatively high vapor pressures. The compounds  $\text{SnCl}_4$  and  $\text{TiCl}_4$  exhibit similar

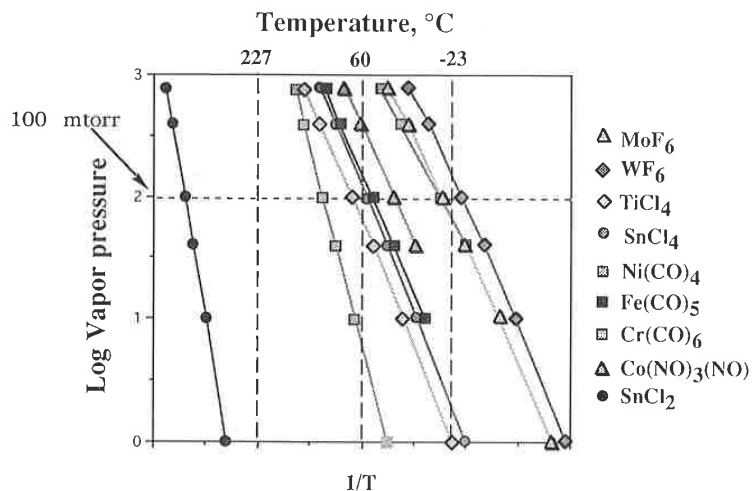


Figure 8-14 Vapor pressures for compounds identified in Table 8-10.

Table 8-10 Temperatures at which Vapor Pressures (mm Hg) are Obtained for Inorganic and Metal-Organic Compounds

Compound	Temperature in °C						m.p.
	1 mm	10 mm	40 mm	100 mm	400 mm	760 mm	
MoF <sub>6</sub>	-65.5	-40.8	-22.1	-8.0	17.2	36.0	17.0
WF <sub>6</sub>	-71.4	-49.2	-33.0	-20.3	1.2	17.3	-0.5
TiCl <sub>4</sub>	-13.9	21.3	48.4	71.0	112.7	136.0	-30.0
SnCl <sub>4</sub>	-22.7	10.0	35.2	54.7	92.1	113.0	-30.2
Ni(CO) <sub>4</sub>	---	---	-23.0	-6.0	25.8	42.5	-25.0
Fe(CO) <sub>5</sub>	---	4.6	30.3	50.3	86.1	105.1	-21.0
Cr(CO) <sub>6</sub>	36.0	68.3	91.2	108.0	137.2	151.0	---
Co(CO) <sub>3</sub> NO	---	---	11.0	29.0	62.0	80.0	-11.0
SnCl <sub>2</sub>	316.0	391.0	450.0	493.0	577.0	623.0	246.8



MoF<sub>6</sub>  
 WF<sub>6</sub>  
 TiCl<sub>4</sub>  
 SnCl<sub>4</sub>  
 Ni(CO)<sub>4</sub>  
 Fe(CO)<sub>5</sub>  
 Cr(CO)<sub>6</sub>  
 Co(NO)<sub>3</sub>(NO)  
 SnCl<sub>2</sub>

l.

ained

760 mm	m.p.
36.0	17.0
17.3	-0.5
36.0	-30.0
13.0	-30.2
12.5	-25.0
15.1	-21.0
51.0	---
30.0	-11.0
23.0	246.8

vapor pressures but lower than those of the fluorides. For comparison to the structural data presented in Figure 8-2, the vapor pressure data for SnCl<sub>2</sub> are shown and are substantially lower compared to SnCl<sub>4</sub>. The monomeric carbonyl compounds all have similar vapor pressures and are in the range observed for the tetrahalides of Sn and Ti. The vapor pressures of a number of metal β-diketonates (Cr, Rh, Al, Fe, Cu, Pd; hfac and fod) are discussed by Wolf et al.<sup>92</sup>

### 8.3 Syntheses

An extensive review of synthetic routes to all the compounds used as CVD precursors is beyond the scope of this book, especially since many of the species studied do not give rise to pure metal films. Many of the compounds used are either commercially available [metal halides, alkyls, allyls, and many of the metal carbonyls, metallocenes, and β-diketonates (see Table 8-4)] or simply prepared in high yield and the reader is directed to standard texts on this subject.<sup>59,60,70,97</sup> Synthetic routes to the compounds that are not commercially available are generally contained in the papers referenced here or references therein.

## 8.4 Chemical Vapor Deposition

### 8.4.1 Deposition Characteristics

#### 8.4.1.1 Introduction

Volatile metal-containing compounds have been used for generation of films by a variety of processes including chemical vapor deposition, large-area photochemically-induced deposition using lamps,<sup>108</sup> focused-laser-induced deposition by photochemical<sup>34,49-51,108,109</sup> and photothermal routes,<sup>34,49-51,108-110</sup> atomic layer epitaxy,<sup>111</sup> chemical beam epitaxy,<sup>112</sup> and others. The precursors used for these approaches are primarily the same as those used for CVD. Extensive literature exists for laser-induced deposition of metals<sup>34,49-51,108-110,113</sup> and will not be covered in this chapter.

This section will discuss metal CVD using the precursors identified in Section 8.2 (see Table 8-1). Emphasis is on the types of precursors used, substrates, temperatures, carrier gases, purities, and rates where known. Section 8.4.2 will focus on kinetics and mechanisms of CVD of these metals where known. In this section each metal is discussed in order of its appearance in the different groups of the Periodic Table.

#### 8.4.1.2 Titanium

Chemical vapor deposition of titanium has not been discussed extensively in the literature, probably due to the difficulty in depositing the pure metal because it is easily oxidized and exposure to oxygen leads to contamination. In the patent literature, however, numerous volatile precursors that provide sources of Ti are claimed, but very little analytical data have been presented to support deposition of high-purity Ti films. A patent by Homer<sup>114</sup> reports that  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$  can be used to deposit Ti, but no purity data were reported. The species  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)$  was used as a precursor for CVD of Ti by others.<sup>115,116</sup> However, even in an  $\text{H}_2$  plasma the films were comprised mainly of C. Other titanium alkyl and aryl compounds such as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiR}_2$ , where  $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ , also decompose to form products which contain considerable amounts of carbon.<sup>117-120</sup> Some examples of Ti deposition are from  $\text{TiCl}_4$ <sup>121</sup> and  $\text{TiBr}_4$ <sup>122</sup> by photochemical reactions or at high temperatures (900 °C) attained by laser heating. The purities reported in these cases were on the order of 90% and the 10% impurities may have been due to exposure to oxygen. Campbell et al. studied the use of  $\text{TiI}_x$  at 1300-1400 °C for generation of Ti metal but did not examine CVD.<sup>123</sup> Chemical vapor deposition of titanium-rich films has also been reported from  $\text{Ti}[\text{tris-(2,2'-bi-pyridine)}]$  at temperatures near 600 °C.<sup>124</sup> The films, however, contained significant amounts of contaminants, up to 35% C, O, N, and H.

#### 8.4.1.3 Zirconium

There have only been a few studies of the CVD of zirconium metal. The "hot-wire" process which involves the thermal decomposition of  $\text{ZrI}_4$  has a reaction efficiency of 0.32 at 1152 °C.<sup>125</sup> The complex  $\text{Zr}(\text{CH}_2\text{-}t\text{-Bu})_4$  deposited crystalline ZrC films above 500 °C with a metal:carbon ratio of 1:2. Carbon X-ray photoelectron spectroscopy (XPS) revealed carbidic carbon, graphitic carbon, and a third unidentified type of carbon species.<sup>126</sup> Thermal decomposition of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrR}_2$ , where  $\text{R} = \text{Me}, \text{C}_6\text{H}_5$ , and  $\text{C}_6\text{F}_5$ , compounds leads to carbon-contaminated products.<sup>117-120, 127</sup>

#### 8.4.1.4 Hafnium

The decomposition of hafnium iodide was used to form hafnium metal.<sup>128</sup> The reaction, carried out at 1100 °C, gave hafnium of unknown purity. Apparently, the CVD of hafnium metal from other precursors has not been reported in the literature, although metal-organic hafnium compounds, such as  $\text{Hf}(\text{O-}t\text{-Bu})_4$ , have been used to deposit Hf-containing films, e.g.,  $\text{HfO}_2$ .<sup>129</sup>

#### 8.4.1.5 Vanadium

Pure vanadium metal is commercially obtained by thermal decomposition of the halides. Pure vanadium and the vanadium alloys V/Nb, V/Ti, and V/Ti/Nb have been

extensively in the because it is easily : patent literature, claimed, but very -purity Ti films. A it Ti, but no purity as a precursor for ns were comprised  $(\eta^5)\text{TiR}_2$ , where R lerable amounts of and  $\text{TiBr}_4$ <sup>122</sup> by laser heating. The 9% impurities may e of  $\text{TiI}_x$  at 1300-

Chemical vapor [2'-bi-pyridine]] at ficant amounts of

al. The "hot-wire" tion efficiency of e ZrC films above pectroscopy (XPS) d type of carbon = Me,  $\text{C}_6\text{H}_5$ , and

n metal.<sup>128</sup> The parently, the CVD iterature, although sed to deposit Hf-

omposition of the /Ti/Nb have been

deposited at temperatures between 850 and 900 °C by thermal decomposition of the halides formed by passing  $\text{Cl}_2$  over metal chips.<sup>130</sup> The films were deposited in the presence of  $\text{H}_2$  and He gases. No low-temperature CVD routes exist. The thermal decomposition of a number of organometallic vanadium compounds including  $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ ,<sup>24</sup>  $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\eta^6\text{-C}_6\text{H}_6)$ ,<sup>120</sup>  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2$ ,<sup>131</sup>  $\text{V}(\text{CO})_6$ ,<sup>132</sup> and  $(\eta^6\text{-C}_6\text{H}_6)_2$ <sup>133</sup> has been reported, but few data are available on the identity of the materials formed.

#### 8.4.1.6 Niobium

Chemical vapor deposition of niobium has been examined primarily in the context of deposition of the superconducting phases  $\text{Nb}_3\text{Ge}$  and  $\text{Nb}_3\text{Ga}$  (Table 8-11). Only the niobium halides have been studied extensively as precursors.<sup>28,29,134-143</sup> As a result, the lowest deposition temperature obtained is near 700 °C. The films are generally of high-purity. In the case of the superconductors  $\text{Nb}_3\text{Ga}$  and  $\text{Nb}_3\text{Ge}$ , excellent electrical properties have been obtained. Niobium and Nb-containing films have been grown primarily from  $\text{NbCl}_5$  in  $\text{H}_2$ . Only a few studies have examined  $\text{NbBr}_5$ . Niobium films have been deposited at 1200 °C at rates of up to 3,000 nm/min using  $\text{NbBr}_5$ .<sup>28</sup> The decomposition of  $\text{Nb}(\eta^6\text{-C}_6\text{H}_6)_2$  has been reported in the patent literature.<sup>133</sup> The CVD of  $\text{Nb}_3\text{Ge}$ <sup>141</sup> and doping of  $\text{TiO}_2$  using Nb ethoxide<sup>140</sup> have also been studied. No low-temperature routes to high-purity Nb films exist.

Table 8-11 Niobium Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
$\text{NbBr}_5$	Graphite	1200-1400	none	high	1000-3000	28, 29
$\text{NbCl}_5$	Ruby, Sapphire	850-900	none	---	---	134
$\text{NbCl}_5^*$	Cu	900	Ar $\text{H}_2$	high	---	135
$\text{NbCl}_5^*$	Si	800-1100	Ar $\text{H}_2$	high	1600	137
$\text{NbCl}_5^*$	$\text{SiO}_2$	720	Ar $\text{H}_2$	high	170-340	138
$\text{NbCl}_5^{**}$	Carbon	600-1200	$(\text{CH}_3)\text{N}$ , Ar, $\text{NH}_3$ , $\text{N}_2$	high	---	139
$\text{NbCl}_5^*$	$\text{SiO}_2$	700-900	He, $\text{H}_2$	high	170	141

\* Deposition of  $\text{Nb}_3\text{Ge}$  or  $\text{Nb}_3\text{Ga}$ .

\*\* Deposition of carbonitride

#### 8.4.1.7 Tantalum

The halide,  $\text{TaCl}_5$ , has been the main source for CVD of tantalum (Table 8-12).<sup>144-149</sup> Although high-purity films have been obtained with  $\text{TaCl}_5$  at rates of 1,000 nm/min using hydrogen as a reducing agent, the primary problem is the need for temperatures greater than 700 °C. Tantalum deposition has also been attempted from  $\text{Ta}(\text{CO})_5$ , but the films contained 5-10% impurities.<sup>150</sup> Ugolini, using XPS, studied the surface chemistry of Ta CVD from  $\text{TaCl}_5$ .<sup>151</sup> This study showed that high-purity Ta could be produced even in the absence of hydrogen. The thermal decomposition of  $\text{Ta}(\eta^6\text{-C}_6\text{H}_6)_2$ <sup>133</sup> and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{C}_6\text{F}_5)_2$ <sup>127</sup> has been reported in the patent literature. Tantalum CVD has also been studied by others.<sup>152</sup> No low-temperature CVD routes to Ta films currently exist.

Table 8-12 Tantalum Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
$\text{TaCl}_5$	Mo	650-1100	$\text{H}_2$ , $\text{N}_2$	high	50-100	144
$\text{TaCl}_5$	Stainless steel	900-1050	$\text{H}_2$	>99%	2000	145
$\text{TaCl}_5$	$\text{SiO}_2$ , $\text{Al}_2\text{O}_3$	800-1500	$\text{H}_2$ , $\text{N}_2$	high	30	146
$\text{TaCl}_5$	$\text{Al}_2\text{O}_3$	up to 1500	Ar, $\text{H}_2$	high	---	147
$\text{TaCl}_5$	Steel	1000	$\text{H}_2$ , $\text{N}_2$	high	2000	148
$\text{TaCl}_5$	Cu, Fe, Ni, Mo	600-1400	$\text{H}_2$ , $\text{N}_2$	high	125	149
$\text{Ta}(\text{CO})_5$	Cu	450-600	$\text{H}_2$	90-95%	---	150
$\text{TaF}_5$	Si, $\text{SiO}_2$	250-400	none	high	---	151

#### 8.4.1.8 Chromium

Chromium or Cr-containing films have been deposited from only a few precursors (Table 8-13). The primary problem is the lack of low-temperature routes to the pure metal. Chromium halides deposit pure metal but require deposition temperatures near 1000 °C. For example,  $\text{CrCl}_2$  deposits pure Cr at temperatures over 800 °C.<sup>66,67,154,155</sup> Other precursors have lower deposition temperatures but impure films result. For example,  $\text{Cr}(\text{CO})_6$  provides deposition temperatures of 400 °C but the films are contaminated with carbon.

able 8-12).<sup>144-149</sup>  
 00 nm/min using  
 peratures greater  
 1)<sup>5</sup>, but the films  
 chemistry of Ta  
 produced even in  
 6)<sup>2</sup><sup>133</sup> and ( $\eta^5$ -  
 m CVD has also  
 currently exist.

Rate nm/min	Ref.
100	144
100	145
30	146
---	147
100	148
25	149
---	150
---	151

few precursors  
 rates to the pure  
 mperatures near  
 °C.<sup>66,67,154,155</sup>  
 ns result. For  
 the films are

Studies of CVD of Cr using organometallic precursors have been motivated by the lack of other precursors which allow low-temperature deposition of high-purity chromium films. However, in general, no organometallic precursors have been successful in depositing pure Cr films. In a cold-wall reactor, ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Cr(CO)<sub>3</sub> deposited carbide and oxide contaminated films above 300 °C.<sup>157</sup> Extensive characterization of the reaction products was performed by gas chromatography and mass spectrometry. Labelling studies showed that most of the carbon was derived from the cycloheptatriene ring with only a minor contribution from the carbonyl ligands (see Section 8.4.2.3).

The precursor Cr(cumene)<sub>2</sub> formed carbide films at 350-520 °C at rates of 4.5-6.5 nm/min in a cold-wall reactor using argon as the carrier gas.<sup>77</sup> The deposition rate exhibited a maximum at 450 °C, but the origin of this observation was not interpreted. The resistivity of the films was high, decreased with temperature, and remained above 100  $\mu\Omega$ cm at 550 °C. The films were used to fabricate high-quality Schottky barrier diodes. Similar results were obtained for Cr( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and other studies with Cr(cumene)<sub>2</sub> which gave films consisting of Cr and Cr<sub>3</sub>C<sub>2</sub>.<sup>159,160</sup>

Table 8-13 Chromium Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
Cr(CO) <sub>6</sub>	Fe, Cu, Steel	400-600	H <sub>2</sub>	---	---	153
Cr(cumene) <sub>2</sub>	Si, SiO <sub>2</sub>	350-520	Ar	C impurity	4.5-6.5	77
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cr(CO) <sub>3</sub> H	Si	330-470	none or H <sub>2</sub>	C+O impurity	---	158
Cr[CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	Si	330-470	none or H <sub>2</sub>	C+O impurity	---	„
Cr(N- <i>i</i> -Pr) <sub>3</sub>	Si	330-470	none or H <sub>2</sub>	C+N impurity	---	„
( $\eta^6$ -C <sub>7</sub> H <sub>8</sub> )Cr(CO) <sub>3</sub>	Glass, Al	300-600	none	28-36% C	---	157
CrCl <sub>2</sub>	Steel	750-1000	H <sub>2</sub>	>99% Cr	100-200	67
CrCl <sub>2</sub>	Steel	970-1100	H <sub>2</sub>	high purity	---	154
CrCl <sub>2</sub>	Ni	950-1050	H <sub>2</sub>	>99% Cr	---	155
CrCl <sub>2</sub>	Nb alloy	900	H <sub>2</sub>	>99% Cr	600-5000	66
CrF <sub>2</sub>	---	950-1050	H <sub>2</sub>	high purity	---	156

Rutherford et al.<sup>158</sup> used several organometallic precursors in a low-pressure cold-wall reactor to examine the deposition of Cr-containing films. Chromium carbide (Cr<sub>3</sub>C<sub>2</sub>) films, produced at temperatures as low as 300 °C, were the prime result of CVD using Cr( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>H, Cr(CH<sub>2</sub>-*t*-Bu)<sub>4</sub>, and Cr(N-*i*-Pr)<sub>3</sub>. In general, higher deposition temperatures led to lower resistivities, and the best of these were in the 200-300  $\mu\Omega$ cm

range. Carrier gas composition ( $H_2$ , Ar, He) had no effect on film properties. Similar behavior was observed for  $Cr(t-Bu)_4$  and other tetraalkyl chromium compounds.<sup>161-163</sup> The best source of chromium carbide films was  $Cr(N-i-Pr)_2$ .

#### 8.4.1.9 Molybdenum

High rates of pure molybdenum film deposition can be obtained at temperatures as low as 200 °C (Table 8-14) using  $MoF_6$ ,  $Mo(CO)_6$ , and  $MoCl_5$ . All of these precursors allow deposition of clean metal under certain conditions. Deposition temperatures for  $MoF_6$  range from 200-500 °C, for  $Mo(CO)_6$  range from 200-600 °C, and for  $MoCl_5$  range from 500 to 1100 °C. Because these precursors are widely available, other precursors have not been extensively examined (see Table 8-14). Using  $M(allyl)_4$  ( $M = Mo$  and  $W$ ) as

Table 8-14 Molybdenum Chemical Vapor Deposition Conditions

Precursor	Substrate	$T_{\text{substrate}}$ °C	Carrier Gas	Purity	Rate nm/min	Ref.
$MoCl_5$	Ni, Glass	800-1100	$H_2$	---	8,350	164
$MoCl_5$	---	500-750	$H_2$	high	---	165
$MoCl_5$	Si	400-1200	$H_2$	>99%	0.1-40	166
$MoCl_5$	Si	500-750	$H_2$	>99%	1-20	167
$MoCl_5$	Si	600-1350	$H_2$	high	---	168
$MoCl_5$	Si	450	$H_2$	---	---	169
$MoCl_5$	Ni/Fe	850-950	$H_2$	---	---	146
$MoCl_5$	Si	500-800	$H_2$	high	8.7-35.0	170
$MoF_6$	$SiO_2$	200-400	Ar, $H_2$	4% O	200	171
$Mo(CO)_6$	$SiO_2/Si$	100	$H_2$ , Ar	C+O impurity	---	172
$Mo(CO)_6$	Steel	400	$H_2$	---	250	27
$Mo(CO)_6$	$SiO_2$	400-550	$H_2$ , $CO_2$ , Ar	>99 %	120-480	173
$Mo(CO)_6$	Graphite	400-600	none	>99 %	1.67-25	29
$Mo(CO)_6$	Ta, Glass	175-250	Ar	C impurity	5-100	174
$Mo(CO)_6$	---	400-750	Ar	C impurity	---	165
$Mo(CO)_6$	Fe, Cu, Steel	350-550	$H_2$	>99%	10,000	153
$(\eta^6-C_6H_6)Mo(CO)_3$	Cu	250-550	$H_2$	5-98%	---	150
$[\eta^6-C_6H_3(CH_3)_3]-Mo(CO)_3$	Cu	250-650	$H_2$	1-100%	---	"
$Mo(\eta^3-allyl)_4$	Pyrex	350-450	$H_2$ or none	low	0.47-1.8	75, 175



properties. Similar compounds.<sup>161-163</sup>

temperatures as low as 170 °C. Similar precursors allow deposition rates for MoF<sub>6</sub> and MoCl<sub>5</sub> range from 0.1 to 100 nm/min. Precursors have not been used for Mo and W) as

Rate nm/min	Ref.
8,350	164
---	165
0.1-40	166
1-20	167
---	168
---	169
---	146
.7-35.0	170
200	171
---	172
250	27
20-480	173
.67-25	29
5-100	174
---	165
0,000	153
---	150
---	"
47-1.8	75, 175

precursors, CVD resulted in the deposition of metal carbides together with amorphous carbon.<sup>75,175</sup>

Kaplan and d'Heurle examined the deposition of Mo films from Mo(CO)<sub>6</sub> in a cold-wall reactor.<sup>173</sup> Films with bulk resistivity were grown at 500 °C at a rate of 22 nm/min using 0.001 torr CO and 0.01 torr H<sub>2</sub>. Films deposited at lower temperatures resulted in higher resistivities, presumably due to higher levels of carbon. The lowest deposition temperature was 170 °C but only films deposited above 450 °C had satisfactory properties. Resistivities decreased with increasing temperature until a critical temperature was reached at which the resistivity became independent of temperature. The decrease in resistivity with temperature was dramatic, a factor of 100 for a temperature change of only 50 °C. This effect was explained in terms of the purity of the films which increased with increasing temperature and emphasizes the importance of deposition temperature in determining film properties. Several approaches were investigated to determine the lowest temperature at which high-purity, low-resistivity films could be produced. Production of high-quality films required temperatures of 500 °C or higher.

Molybdenum films can also be obtained by MoF<sub>6</sub> reduction on silicon substrates in the presence of hydrogen (see also Ch. 3).<sup>171</sup> Deposition is the result of both the reaction with Si and with H<sub>2</sub> in roughly equal ratios. High deposition rates of 200 nm/min were obtained in the low-pressure, hot-wall reactor and no self-limiting thickness was observed. However, the films were highly porous (30%) due to diffusion of the precursor through the film to the Mo/Si interface where reaction to form Mo occurred. The extensive porosity led to a high surface area which resulted in oxygen contamination (4%) when exposed to air even at room temperature.

As a result of the porosity and oxygen contamination, the resistivities of the films were an order of magnitude higher than bulk. The morphology of films produced by this approach makes this a poor method for Mo film deposition.

The precursor MoCl<sub>5</sub>, in the presence of hydrogen, has been used extensively for deposition of molybdenum films. Sugano et al.<sup>166</sup> have shown that high-purity films with nearly bulk resistivity can be formed between 600 and 800 °C in a cold-wall reactor. The deposition rate was investigated as a function of temperature and exhibited a maximum at 600 °C. The deposition rate was first order in MoCl<sub>5</sub> concentration. The resistivity decreased with increasing temperature until roughly 600 °C where it became constant. Yasuda and Murota<sup>167</sup> studied MoCl<sub>5</sub> reduction by hydrogen in a hot-wall reactor. Diffusion-limited deposition (see Ch. 9) was observed above 600-700 °C. The reaction rate was proportional to the 3/2 power of the hydrogen partial pressure.

Other investigations of Mo CVD not listed in Table 8-14 include the thermodynamics of selective CVD,<sup>176</sup> the generation of MoS<sub>2</sub> using bromine transport,<sup>177</sup> and CVD using Mo(CO)<sub>6</sub>.<sup>178</sup> Wlodek and Wulff<sup>179</sup> have used MoCl<sub>5</sub> to coat surfaces at 900 °C. Molybdenum-silicon Schottky barriers have been prepared by CVD using MoCl<sub>5</sub>.<sup>180</sup> The compound Mo(PF<sub>3</sub>)<sub>6</sub> produced high purity Mo films, analogous to W(PF<sub>3</sub>)<sub>6</sub><sup>84</sup> (see Ch. 3). However, as described earlier, the potential for impurity incorporation exists when PF<sub>3</sub> is liberated.

#### 8.4.1.10 Manganese

The deposition of Mn films, apparently, has not been investigated in any detail, although Mn-Si films have been produced using single-source heterometallic precursors (see Sections 8.4.1.23 and 8.4.2.7). Manganese-containing coatings have been obtained by pyrolysis of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}$  at 460 °C in a glass vessel.<sup>131</sup> The photodissociation of  $\text{Mn}_2(\text{CO})_{10}$  at wavelengths of 193-351 nm has been studied suggesting laser-induced deposition is possible.<sup>181-183</sup>

#### 8.4.1.11 Technetium

Although technetium is not a naturally occurring element, its chemical attributes are useful for radiopharmaceutical applications. Technetium CVD has not been reported in the open literature.

#### 8.4.1.12 Rhenium

Chemical vapor deposition of rhenium has not been studied extensively (see Table 8-15). The precursors  $\text{ReF}_6$ ,  $\text{ReCl}_5$ ,  $\text{HRe}(\text{CO})_5$ , and  $\text{Re}_2(\text{CO})_{10}$ <sup>184-188</sup> have been used primarily in conjunction with  $\text{WF}_6$  to deposit tungsten-rhenium alloys. The purity of the deposited alloy films was high in all cases except for  $\text{HRe}(\text{CO})_5$ . The compound  $\text{Re}_2(\text{CO})_{10}$  deposits films onto substrates heated to temperatures between 400 and 600 °C. A maximum in deposition rate was observed at 500 °C; however, no characterization data were presented so the purity of the films is unknown. No precursors exist for CVD of high-purity Re metal at low-temperatures (< 400 °C), although Re has been deposited by PECVD using  $(\text{CH}_3)_3\text{Re}(\text{CO})_5$  and  $\text{HRe}(\text{CO})_5$ . Several other discussions of rhenium CVD are available.<sup>189-191</sup> For example, Aylett et al.<sup>191</sup> have used  $\text{HRe}(\text{CO})_5$  to deposit Re on porous Si substrates.

Table 8-15 Rhenium Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
$\text{ReF}_6$	Mo	500-1000	$\text{H}_2$	high	4,200 to 12,000	184, 185
$\text{ReF}_6$	$\text{Al}_2\text{O}_3$	1000-1500	$\text{H}_2$	high	---	186
$\text{ReF}_6$	Cu	200-800	$\text{H}_2$	high	---	187
$\text{HRe}(\text{CO})_5$	$\text{SiO}_2$ , Si	130	$\text{H}_2$ , Ar	30% C + O	---	188



## 8.4.1.13 Iron

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ing laser-induced

Precursors for CVD of iron allow deposition of high-purity films at temperatures as low as 200 °C at high rates (Table 8-16). The majority of studies used iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , as a precursor. Ferrocene,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ , has been studied to a lesser extent because it requires higher deposition temperatures near 400 to 500 °C, consistent with its higher thermal stability. Iron halides have been studied to a much lesser extent due to their deposition temperatures of 1000 °C.

Table 8-16 Iron Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
$\text{FeF}_3$	---	750-1150	none	>99%	---	<b>192</b>
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	Steel rod	550-600	none	---	0.3	<b>193</b>
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	Si	400-900	He, $\text{H}_2$	>99%	---	<b>31</b>
$\text{Fe}(\text{CO})_5$	GaAs	200	none	>99%	0.5	<b>194</b>
$\text{Fe}(\text{CO})_5$	GaAs	150-300	$\text{H}_2$	>99%	20	<b>195</b>
$\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4$	Si, Glass	260-310	He	3% C + O	8.4	<b>196</b>

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Kaplan and Bottka deposited epitaxial films of Fe onto GaAs using  $\text{Fe}(\text{CO})_5$  at 200 °C with deposition rates of 0.5 nm/min in an ultra-high-vacuum (UHV) system.<sup>194</sup> Excellent film quality was observed by LEED (low energy electron diffraction) and AES (Auger electron spectroscopy). The films had comparable quality to films grown by MBE (molecular beam epitaxy). Films grown on GaAs proceeded by layer rather than island growth mechanisms. Walsh and Bottka<sup>195</sup> extended this approach to deposition of Fe films onto GaAs using  $\text{Fe}(\text{CO})_5$  at substrate temperatures of 150 to 300 °C and deposition rates of 0.3 nm/min in a conventional CVD system using hydrogen as the carrier gas. The optimum temperature for deposition was 200 °C as in the UHV experiments. The films were of high purity, strongly adherent, and showed no indication of tarnishing with time.

Stauf et al. deposited Fe films from  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  at 500-600 °C at rates of 0.3 nm/min using a low precursor partial pressure ( $4 \times 10^{-5}$  torr).<sup>193</sup> The films were strongly adherent to the steel and nickel substrates. No major impurities were observed, but no analysis for carbon and oxygen was carried out. A more extensive study with  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  was carried out by Dormans who deposited  $\alpha\text{-Fe}$  with atmospheric pressure  $\text{H}_2$  carrier gas at temperatures of 400 to 900 °C.<sup>31</sup> Auger electron spectroscopy depth profiles showed no detectable carbon and oxygen. Interestingly, no deposition was

Rate m/min	Ref.
200 to 2,000	<b>184, 185</b>
---	<b>186</b>
---	<b>187</b>
---	<b>188</b>

observed in He up to 900 °C for the Si substrates. A similar inhibition was observed for  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$  suggesting that the effect was more general and not specific to ferrocene. This type of selectivity has not been studied or exploited for applications.

A binuclear compound,  $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4$ , has also been examined (see Fig. 8-8)<sup>196</sup> This precursor was used to deposit films at up to 8.4 nm/min at temperatures of 260-310 °C on a Si(111) substrate and glass plates. The films contained 97% Fe with small amounts of C and O, but the source of the contamination was not identified.

#### 8.4.1.14 Ruthenium

Chemical vapor deposition of Ru has been investigated in only a few cases (Table 8-17). Deposition temperatures as low as 250 °C with adequate rates and high purity have been obtained. The best films have been produced from  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Ru}(\text{hfb})(\text{CO})_4$  where hfb = hexafluoro-2-butyne. The volatile  $\text{Ru}(\text{CO})_5$  has poor thermal stability which limits its use. Little data are available on film properties obtained using  $\text{Ru}(\text{acac})_2$ .<sup>35,199</sup> Ruthenium has been deposited from ruthenocene,  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$ , in  $\text{H}_2$  above 500 °C.<sup>35,197</sup> Precursors which allow deposition below approximately 300 °C are not available.

Table 8-17 Ruthenium Chemical Vapor Deposition Conditions

Precursor	Substrate	$T_{\text{substrate}}$ °C	Carrier Gas	Purity	Rate nm/min	Ref.
$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$	Vycor	600	$\text{H}_2$	>99%	---	197
$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$	$\text{SiO}_2$	500-800	$\text{H}_2$ , $\text{O}_2$	>80%	---	35
$\text{Ru}_3(\text{CO})_{12}$	$\text{SiO}_2$	250-400	Vacuum $\text{H}_2$ , $\text{O}_2$	>99%	---	35
$\text{Ru}(\text{acac})_2$	$\text{SiO}_2$	500-600	Vacuum $\text{H}_2$ , $\text{O}_2$	>99%	---	35
$\text{Ru}(\text{hfb})(\text{CO})_4$	$\text{SiO}_2$	500	none, $\text{H}_2$	>80% >99%	60	198

Deposition of ruthenium films on silicon has been accomplished using  $\text{Ru}(\text{hfb})(\text{CO})_4$  in a hot-wall reactor.<sup>198</sup> The high volatility of this precursor (1-2 torr at room temperature) allowed deposition without a carrier gas. High-purity films were deposited which had good adhesion and were smooth and highly reflective.

The precursor  $\text{Ru}_3(\text{CO})_{12}$  allowed deposition of high-purity films with resistivities of 17  $\mu\Omega\text{cm}$  at temperatures of 300 °C under vacuum in a hot-wall reactor.<sup>35</sup> The films had

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<sup>35</sup> The films had

excellent adhesion to Si and SiO<sub>2</sub> substrates. The precursor Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> also allowed high-purity film formation. Interestingly, films could only be deposited from Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> in oxygen. The same precursor was used to deposit RuO<sub>2</sub> films which have useful properties similar to Ru films. The best RuO<sub>2</sub> film deposited using Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> in O<sub>2</sub> at 575 °C had a resistivity of 90  $\mu\Omega$ cm. The films were adherent and specular. The precursor Ru(acac)<sub>2</sub> provided films with high resistivities and with high carbon content even in the presence of hydrogen.<sup>35</sup>

#### 8.4.1.15 Osmium

Very little work has been done with CVD of osmium. The precursor OsCl<sub>4</sub>, however, has been used to deposit Os onto Mo and W substrates at temperatures of 1250 °C at pressures of  $5 \times 10^{-3}$  torr.<sup>200</sup> The precursor Os(hfb)(CO)<sub>4</sub> has been used to deposit Os films and is analogous to the precursor Ru(hfb)(CO)<sub>4</sub>.<sup>198</sup>

#### 8.4.1.16 Cobalt

High-purity cobalt films can be deposited at temperatures as low as 200 °C at high rates (Table 8-18). Several precursors, including Co<sub>2</sub>(CO)<sub>8</sub>, Co(acac)<sub>2</sub>, and Co( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> allow deposition at temperatures near 200-300 °C. Other precursors that have been used to form films containing Co include Co(NO)(CO)<sub>3</sub> for doping InGaAsP,<sup>37</sup> CoCl<sub>2</sub> for deposition of CoB and CoSi<sub>2</sub>,<sup>205,206</sup> and Co<sub>4</sub>(CO)<sub>12</sub> for deposition of cobalt.<sup>82</sup>

Table 8-18 Cobalt Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
Co( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	Si	300-700	H <sub>2</sub> , He	>99%	0.6-60	<b>201</b>
Co(acac) <sub>2</sub>	Glass	324-352	H <sub>2</sub>	high	100	<b>202</b>
Co(acac) <sub>2</sub>	Quartz	275-310	H <sub>2</sub>	>99%	---	<b>100</b>
Co <sub>2</sub> (CO) <sub>8</sub>	Si	60-450	Ar	>99.5%	10	<b>203, 204</b>
HCo(CO) <sub>4</sub>	Si	60-450	Ar	>99.5%	10	" "
Co <sub>2</sub> (CO) <sub>8</sub>	Si, SiO <sub>2</sub>	200-400	none	>99%	5.0	<b>30</b>
Co( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	Si	200-900	H <sub>2</sub> , He	>99%	3.6	<b>201</b>
Co <sub>2</sub> (CO) <sub>8</sub>	Si	150-400	" "	>99%	3	"
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Co(CO) <sub>2</sub>	Si	300-600	" "	>99%	240	"
(CF <sub>3</sub> )Co(CO) <sub>4</sub>	Si	250-750	" "	>99%	0.18	"

Films were deposited from  $\text{Co}_2(\text{CO})_8$  at temperatures of 200-400 °C at rates of 3 nm/min in a hot-wall reactor.<sup>30,203,204</sup> Auger electron spectroscopy analysis of the films deposited at 200 °C showed only surface contamination by carbon, chlorine, and oxygen. Films deposited at higher temperatures had higher impurity concentrations. The films had excellent adhesion, were conformal, and little interdiffusion with the Si substrate was observed by Rutherford Backscattering Spectroscopy (RBS) analysis. The resistivities were 8-20  $\mu\Omega\text{cm}$  which compare well with films produced by other methods. Heating the films resulted in reaction with the silicon substrate to form  $\text{CoSi}_2$ . Dormans et al.<sup>201</sup> observed an upper limit for the deposition temperature using the same precursor which was fixed by the onset of gas phase particle formation in an atmospheric pressure reactor (see Ch. 9).<sup>31</sup> This problem has been avoided by using low pressures for deposition.<sup>30</sup>

The compound  $\text{Co}(\text{acac})_2$  gave films of Co at temperatures from 275 to 430 °C in a hot-wall reactor.<sup>100</sup> Films deposited in the presence of  $\text{H}_2$  had less than 0.5% C and less than 0.2% O. Hydrogen was essential for the reduction to form pure cobalt. The optimum temperature was 275 to 310 °C which was lower than 318 to 350 °C as was suggested by Jablonowski.<sup>202</sup> Feed-rate-limited deposition or transport-limited deposition (see Ch. 9) was observed above approximately 250 °C because of the large reaction area. A patent also discusses the use of cobalt  $\beta$ -diketonate compounds.<sup>89</sup>

The precursor  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$  gave Co films at temperatures of 400-700 °C in hydrogen carrier gas in a cold-wall reactor.<sup>31,201</sup> The growth rate was first order in reactant partial pressure and practically independent of temperature, suggesting feed-rate or mass-transport-limited deposition. Deposition rates of 0.6 nm/min were obtained for a precursor partial pressure of 40 mtorr. The films contained no C or O contamination as determined by AES. When the  $\text{SiO}_2$  was removed from the Si substrate, no deposition was observed at temperatures up to 900 °C in helium. This illustrates the importance of surface cleaning procedures in providing reproducible selectivity and deposition.

The compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and  $(\text{CF}_3)\text{Co}(\text{CO})_4$  gave deposition rates of up to 0.18 nm/min in  $\text{H}_2$  at temperatures of 300-600 °C in a cold-wall reactor.<sup>201</sup> The precursors  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and  $(\text{CF}_3)\text{Co}(\text{CO})_4$  deposited high-purity Co in  $\text{H}_2$  as shown by AES. Deposition in He resulted in high carbon content. Experiments with  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  in helium gave deposition in contrast to results with  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$  where no deposition was observed. This demonstrated the role of precursor design in selective deposition. The deposition rates for  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and  $(\text{CF}_3)\text{Co}(\text{CO})_4$  decreased with increasing temperature due to gas-phase reaction and particle formation as occurred for  $\text{Co}_2(\text{CO})_8$ . This problem was eliminated by using lower pressures of the hydrogen carrier gas.

A number of other precursors have been studied but in less detail. The precursor  $\text{HCo}(\text{CO})_4$  has been used to deposit  $\text{CoSi}_2$  by reaction with an Si substrate.<sup>201</sup>

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#### 8.4.1.17 Rhodium

Several organometallic precursors have been used to deposit Rh metal at temperatures as low as 100 °C at high rates (Table 8-19). These precursors provide sufficient deposition rates and low enough deposition temperatures for most applications. Although several reports exist in the literature, few in-depth studies are available. Little information exists for deposition rates, resistivities, film morphology, and other properties. The surface chemistry of tris(η<sup>3</sup>-allyl)rhodium<sup>105,209,210</sup> and (acac)Rh(CO)<sub>2</sub><sup>211</sup> has been studied on TiO<sub>2</sub> mainly in connection with the catalytic behavior of Rh. The CVD of Rh from (hfac)Rh(1,5-COD) has been reported in a patent although few experimental details are available.<sup>212</sup> A comparison of the CVD of the precursors Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>, Rh(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>, Rh(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(1,5-COD), Rh(η<sup>3</sup>-allyl)(CO)<sub>2</sub>, and Rh(η<sup>3</sup>-allyl)<sub>3</sub> under vacuum (10<sup>-3</sup> torr) and in the presence of H<sub>2</sub> was reported.<sup>213</sup> Although films deposited under vacuum were significantly contaminated with C and O, the presence of H<sub>2</sub> gave rise to 90% pure Rh films. The LCVD of Rh from (hfac)Rh(CO)<sub>2</sub> has produced lines with resistivities of 4.5 μΩcm.<sup>214</sup>

Table 8-19 Rhodium Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity %	Rate nm/min μg/(cm <sup>2</sup> min)	Ref.
Rh(CO) <sub>2</sub> (acac)	Glass	20-150	Ar, H <sub>2</sub>	C+O 2-20	0.4-1.1	103
Rh(CO) <sub>2</sub> (acac)	TiO <sub>2</sub> /Si	200-500	none	C+O impurity	---	105
(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Rh(η <sup>2</sup> -C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	Quartz Glass Si	25	He, H <sub>2</sub>	>99	---	207
[(PF <sub>3</sub> ) <sub>2</sub> RhCl <sub>2</sub> ] <sub>2</sub>	Pyrex	200	none	Cl	120	208
Rh(tfa) <sub>3</sub>	Glass Steel	250	Ar, H <sub>2</sub>	high	---	101
Rh(η <sup>3</sup> -allyl) <sub>3</sub>	Glass	250	Ar, H <sub>2</sub>	>97 in H <sub>2</sub> plasma >86 in vacuum	0.3-7.3	74
Rh(η <sup>3</sup> -allyl) <sub>3</sub>	SiO <sub>2</sub>	120	Ar, H <sub>2</sub>	>98	---	188

continued

Table 8-19 continued

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity %	Rate nm/min	Ref.
Rh( $\eta^3$ -allyl) <sub>3</sub>	SiO <sub>2</sub>	180	none	Rh 86 C 4 O 0	~33	213
	SiO <sub>2</sub>	130	H <sub>2</sub>	Rh 96 C 14 O 0	~33	213
	SiO <sub>2</sub>	180	none	Rh 49 C 24 O 27	~33	213
Rh <sub>2</sub> (Cl) <sub>2</sub> (CO) <sub>4</sub>	SiO <sub>2</sub>	180	H <sub>2</sub>	Rh 91 C 7 O 2	~33	213
	SiO <sub>2</sub>	180	none	Rh 75 C 20 O 5	~33	213
	SiO <sub>2</sub>	180	H <sub>2</sub>	Rh 89 C 7 O 4	~33	213
Rh( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub>	SiO <sub>2</sub>	270	none	Rh 81 C 19 O 0	~33	213
	SiO <sub>2</sub>	230	H <sub>2</sub>	Rh 97 C 3 O 0	~33	213
	SiO <sub>2</sub>	180	none	Rh 48 C 40 O 12	~33	213
Rh( $\eta^3$ -allyl)(CO) <sub>2</sub>	SiO <sub>2</sub>	180	H <sub>2</sub>	Rh 94 C 6 O 0	~33	213

#### 8.4.1.18 Iridium

Several metal-organic precursors have been used to deposit Ir at temperatures as low as 100 °C with reasonable rates and high purity (Table 8-20). In addition to the precursors shown in the Table, Ir(acac)<sub>3</sub> has been used for CVD,<sup>216</sup> and the use of Ir( $\beta$ -diketonate)<sub>3</sub> precursors has also been discussed in a patent,<sup>217</sup> but little quantitative information is available about the use of these precursors for CVD.

Table 8-20 Iridium Chemical Vapor Deposition Conditions

Rate m/min	Ref.	Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity %	Rate nm/min	Ref.
~33	213	IrCl <sub>3</sub>	Graphite	825-975	H <sub>2</sub> , CO, Ar	high	---	68
		IrCl <sub>4</sub>	Graphite	825	H <sub>2</sub> , CO, Ar	high	---	"
		IrBr <sub>3</sub>	Graphite	825	H <sub>2</sub> , CO, Ar	high	---	"
~33	213	IrF <sub>6</sub>	Graphite	725-875	H <sub>2</sub> , CO, Ar	high	200	"
		Ir( $\eta^3$ -allyl) <sub>3</sub>	SiO <sub>2</sub>	100	H <sub>2</sub>	>98%	---	188
~33	213	Ir( $\eta^3$ -allyl) <sub>3</sub>	Glass	250-450	H <sub>2</sub> , Ar, vacuum	3-17% C	0.1-3.3	74
		Ir(acac)(1,5-COD)	Cu	400-750	H <sub>2</sub>	85-99%	---	150
~33	213	{(COD)Ir[ $\mu$ -OCH <sub>3</sub> ]} <sub>2</sub>	Cu	600	H <sub>2</sub>	90-95%	---	"
		( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> )Ir(1,5-COD)	Quartz	120-680	H <sub>2</sub> , vacuum	>99%	1.3-1.4	215
		( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Ir(1,5-COD)	Quartz	"	" "	>99%	"	"
~33	213	(1,5-COD)Ir( $\mu$ -OAc) <sub>2</sub>	Quartz	"	" "	>99%	"	"

Macklin and Withers showed that IrCl<sub>3</sub>, IrCl<sub>4</sub>, IrBr<sub>3</sub>, and IrF<sub>6</sub> allow CVD of high-purity Ir films but at temperatures near 800 °C.<sup>68</sup> Based on its high deposition rate in the warm-wall reactor system, IrF<sub>6</sub> was the best precursor for film deposition. In addition, IrF<sub>6</sub> is a gas at room temperature which makes introduction into the reactor more reliable and reproducible. Carbon monoxide was important in increasing deposition rates and reducing the temperature required for deposition. The role of CO was probably to coordinate with the iridium halides to form intermediate carbonyl halide species, especially in the cases of IrCl<sub>3</sub>, IrCl<sub>4</sub>, and IrBr<sub>3</sub>.

One of the most complete studies of Ir CVD was carried out by Hoke et al. who examined ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)Ir(1,5-COD), ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(1,5-COD), and [(1,5-COD)Ir( $\mu$ -OAc)]<sub>2</sub> as precursors.<sup>215</sup> The motivation for this work was that Ir halides, [(1,5-COD)Ir( $\mu$ -OCH<sub>3</sub>)]<sub>2</sub>, Ir(acac)(1,5-COD), and Ir(acac)<sub>3</sub>, require deposition temperatures above 500 °C, and in many cases they produce films with measurable impurity levels. In contrast, ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)Ir(1,5-COD) and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(1,5-COD) allow deposition of high-purity Ir films at temperatures as low as 120 °C in H<sub>2</sub>. The advantage of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)Ir(1,5-COD) is its low melting point, 40 °C, which makes it available as a liquid source. However, deposition in vacuum leads to films heavily contaminated with carbon. This result can be explained by the low oxophilicity of Ir (the oxide is not stable below 550 °C) which allows deposition in the presence of O<sub>2</sub> which serves to oxidize organic species on the surface and convert them into volatile species which can then desorb from the surface.

temperatures as low as  
to the precursors  
Ir( $\beta$ -diketonate)<sub>3</sub>  
ve information is



#### 8.4.1.19 Zinc

The CVD of pure Zn has not been studied in detail. However, a number of studies have examined deposition of zinc as a component of or dopant in materials such as ZnS, InGaAlP, GaAs, and  $\text{Zn}_3\text{P}_2$ .<sup>218-227</sup> The precursors that have been used most successfully are  $\text{Zn}(\text{CH}_3)_2$  and  $\text{ZnEt}_2$ . In addition, the surface reactions of zinc alkyls on Si(100) surfaces have been investigated.<sup>228</sup> The laser-induced CVD of Zn from  $\text{Zn}(\text{CH}_2\text{CH}_3)_2$  has also been achieved.<sup>113</sup>

#### 8.4.1.20 Cadmium

The majority of the work on Cd is for deposition of multicomponent materials where Cd is one component such as in CdS and (Cd,Hg)Te, laser deposition, and as a dopant in materials such as InP.<sup>229,230</sup> The precursors that have been used most extensively are  $\text{Cd}(\text{CH}_3)_2$  and  $\text{CdEt}_2$ . Little information exists for CVD of pure Cd.

#### 8.4.1.21 Tin

Chemical vapor deposition of tin has not been studied extensively.<sup>231</sup> However, tin has been formed from  $\text{SnH}_4$ ,  $\text{Sn}(\text{CH}_3)_4$ ,  $\text{Sn}(-n\text{-Bu})_4$ ,  $\text{EtSnH}_3$ , and  $\text{Br}_2\text{Sn}(-n\text{-Bu})_2$ , and the kinetics of  $\text{SnH}_4$  decomposition has been studied in detail (see Section 8.4.2.2). Few data are available for the other species. Most results in the literature are given for laser-induced deposition<sup>113,232-234</sup> as a component of superconductors ( $\text{Nb}_3\text{Sn}$ ),<sup>235</sup> as a component in polymer films,<sup>236</sup> and for incorporation of Sn as a dopant into materials such as  $\text{In}_2\text{O}_3$ ,<sup>237,238</sup> GaAs,<sup>239,240</sup> and InAs.<sup>241</sup> Price and Trotman-Dickenson have studied the decomposition of  $(\text{CH}_3)_2\text{SnCl}_2$  at temperatures between 554 and 688 °C but did not attempt CVD.<sup>242</sup> Tin has also been deposited by the pyrolysis of  $(\text{CH}_3)_2\text{SnH}_2$  or  $\text{Sn}_2\text{Et}_6$  at 540 °C using  $\text{CO}_2$  as a carrier gas.<sup>243</sup> A patent also reports CVD using  $\text{Sn}(\text{CH}_3)_4$ ,  $(\text{CH}_3)\text{SnH}_3$ ,  $(\text{CH}_3)_2\text{SnH}_2$ , and  $\text{SnH}_4$ .<sup>244</sup> Gonser and Slowter have also studied CVD of Sn.<sup>245</sup>

#### 8.4.1.22 Lead

Little information exists on CVD of lead. Only a few results are available and these are for photon-induced processes. In these cases, Pb has been deposited primarily from lead alkyls such as  $\text{PbEt}_4$ . Rigby<sup>246</sup> and Chiu et al.<sup>247</sup> reported the photodeposition of lead from  $\text{PbEt}_4$  at room temperature. Other sources of Pb include  $\text{PbPh}_4$ <sup>248</sup> and  $\text{Pb}(\beta\text{-diketonate})_2$ ,<sup>249</sup> but in these cases the Pb is usually incorporated into other materials such as  $\text{PbTiO}_3$  and Pb-Bi-Sr-Ca-Cu-O ceramic superconductors.



## 8.4.1.23 Heterometallic Systems

number of studies  
rials such as ZnS,  
been used most  
s of zinc alkyls on  
VD of Zn from

it materials where  
and as a dopant in  
st extensively are

The use of heterometallic precursors for CVD of metal films has not been studied extensively, and little information is available about film purity and deposition rates. Much more work has been done for materials such as 13-15 (GaAs), 14-16 (ZnSe), and other semiconductors.<sup>250</sup> Table 8-21 shows results for metals. The primary problem with this approach, in addition to the same problems found for simple precursors, is finding precursors with high vapor pressures and deposition rates while maintaining the stoichiometry of the precursor in the film. Existing heterometallic precursors provide low deposition rates and do not always provide controlled stoichiometries in the films.

Liu et al. reported photochemical vapor deposition from  $(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_2\text{Co}(\text{CO})_9$ ,  $\text{HFeCo}_3(\text{CO})_{12}$ , and  $(\eta^5\text{-C}_5\text{H}_5)\text{FeNi}(\text{CO})_3$  which gave Fe-Co and Fe-Ni films.<sup>251</sup> The precursors  $(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$  and  $\text{HFeCo}_3(\text{CO})_{12}$  provided deposition rates of 3.3 and 0.8 nm/min with a substrate temperature of roughly 50 °C and

Table 8-21 Heterometallic Chemical Vapor Deposition Conditions

Precursor	Substrate	T <sub>substrate</sub> °C	Carrier Gas	Purity	Rate nm/min	Ref.
$(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$	Al, Si	50	CO	4 % C	3	251
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_2\text{Co}(\text{CO})_9$	Al, Si	50	CO	---	---	"
$\text{HFeCo}_3(\text{CO})_{12}$	Al, Si	50	CO	---	0.8	"
$(\eta^5\text{-C}_5\text{H}_5)_2\text{FeNi}(\text{CO})_3$	Al, Si	50	CO	---	---	"
$(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$	---	670-770	He	---	---	252, 253
$(\text{H}_3\text{Si})\text{Co}(\text{CO})_4$	---	670-770	He	---	---	" "
$\text{Mn}(\text{CO})_5(\text{SiH}_3)$	---	670-770	He	---	---	" "
$\text{H}_3\text{SiRe}(\text{CO})_5$	---	670-770	He	---	---	" "
$\text{HFeCo}_3(\text{CO})_{12}$	Glass	300-350	CO	>99%	1.7	254
$(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$	Glass	300-350	CO	>99%	1.7	"
$(\text{CO})_4\text{CoGaCl}_2(\text{THF})$	Si, glass	500	H <sub>2</sub>	12% C+O+N	---	48, 255
$\text{R}_2\text{GeMn}_2(\text{CO})_{10}$	SiO <sub>2</sub>	250-500	none, H <sub>2</sub>	<20% C or O	50	256
$[\text{Mn}(\text{CO})_5]_2\text{SiH}_2$	Ni	225-500	none	9-24% O, 18-76% C	60	257, 258
$\text{L}(\text{CO})_n\text{M-ER}^1\text{R}^2(\text{D})$	Si	200-400	---	---	<16	259

where

L = CO,  $\eta^5\text{-C}_5\text{H}_5$ ,  $\text{P}(\text{CH}_3)_3$ ; n = 1-4; M = Mn, Fe, Co, Ni; E = Al, Ga, In; R<sup>1</sup> or R<sup>2</sup> = H or alkyl;  
D = O or N donor ligand.

231 However, tin  
n(-n-Bu)<sub>2</sub>, and the  
8.4.2.2). Few data  
e given for laser-  
(Nb<sub>3</sub>Sn),<sup>235</sup> as a  
ant into materials  
n-Dickenson have  
54 and 688 °C but  
of (CH<sub>3</sub>)<sub>2</sub>SnH<sub>2</sub> or  
ports CVD using  
slower have also

available and these  
ted primarily from  
photodeposition of  
Ph<sub>4</sub><sup>248</sup> and Pb(β-  
ther materials such

were some of the few documented examples of high-purity films. No deposition was observed in the absence of irradiation by the mercury arc lamp. The stoichiometry of the precursor could be maintained in the films.

The precursors  $(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$ ,<sup>254</sup>  $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ ,  $(\text{H}_3\text{Si})\text{Mn}(\text{CO})_5$ ,  $(\text{H}_3\text{Si})\text{Co}(\text{CO})_4$ ,<sup>252,253</sup>  $\text{HFeCo}_3(\text{CO})_{12}$ ,<sup>254</sup> and  $(\text{CO})_4\text{CoGaCl}_2(\text{THF})$ <sup>47,48,255,260,261</sup> have also been examined. Deposition rates were not reported for most of these precursors. For example,  $\text{HFeCo}_3(\text{CO})_{12}$  deposited films at temperatures of 300-350 °C with rates of 1.7 - 2.5 nm/min.<sup>254</sup>

The CVD of manganese germanide and cobalt germanide films from  $\text{R}_2\text{GeBr}_x[\text{M}(\text{CO})_n]_{2-x}$  ( $\text{M} = \text{Mn}, \text{Co}, x = 0,1$ ) has been examined, and AES data showed that films deposited over the temperature range of 250 to 400 °C retained the Ge:M stoichiometry.<sup>256</sup> However, the films were contaminated by carbon.

Fischer<sup>259</sup> used several compounds in the family  $\text{L}(\text{CO})_n\text{MER}^1\text{R}^2(\text{D})$  (where M and E are metals) to deposit films of CoAl, CoGa, CoIn, NiIn, NiAl, NiGa, MnGa, and MnIn. These precursors are either low-melting solids or liquids with vapor pressures of 10-50 mtorr at room temperature. The metal ratio in the precursor could be retained in the films in some cases, but not in others. Deposition temperatures were 200 to 400 °C and rates of up to 16 nm/min were obtained.

## 8.4.2 Kinetics and Mechanisms

Determination of the reaction byproduct distribution and the overall stoichiometry is important in understanding the pathways which lead to pure metal deposition. Unfortunately, there is a paucity of information on the identity of the reaction products for most systems. Only a few systems have been studied in sufficient detail to even allow identification of the main reaction products.

This section discusses the different classes of precursors that have been used for metal deposition according to the nature of the ligands and are discussed in the following order: halides, alkyls, alkene and alkyne  $\pi$ -complexes, allyls, metallocenes, carbonyl  $\pi$ -complexes, trifluorophosphine complexes, metal  $\beta$ -diketonates, bi- and multi-nuclear, and heteronuclear precursors. The composition of the product films is also examined because it relates to the reaction pathways and byproduct distributions. These discussions establish a basis for comparison and allow for rational and systematic design of new CVD precursors.

### 8.4.2.1 Metal Halides

Metal halides in the presence of  $\text{H}_2$  or some other reducing agent (which may be the substrate) and without reducing agents at high temperatures allow deposition of pure metals. Deposition has been investigated from virtually all the metal halides. The main

deposition was  
stoichiometry of the

$\text{H}_3\text{SiMn}(\text{CO})_5$ ,  
17,48,255,260,261

most of these  
s of 300-350 °C

n  $\text{R}_2\text{GeBr}_x$ [Mn-  
owed that films  
ned the Ge:M

(where M and E  
nGa, and MnIn.  
ssures of 10-50  
ined in the films  
) °C and rates of

stoichiometry is  
etal deposition.  
action products  
ail to even allow

n used for metal  
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carbonyl  $\pi$ -com-  
nuclear, and he-  
nined because it  
ssions establish  
new CVD pre-

hich may be the  
osition of pure  
lides. The main

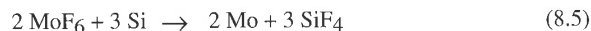
problems with using metal halides as CVD precursors are the low volatility of many of the metal chlorides (see Section 8.2.2.1) and their high thermal decomposition temperatures.

Three deposition mechanisms are possible: (i) reduction by a gas such as  $\text{H}_2$  or  $\text{SiH}_4$ , (ii) reduction via reaction with the substrate (Si for example) to form the metal and another halide species ( $\text{SiCl}_4$ , for example), and (iii) reaction at high temperatures without a reducing agent to form the metal and the corresponding halogen. These approaches are discussed in detail for W in Chapter 3. Examples of these classes of mechanisms are given below.

An example of the first mechanism is the reaction of  $\text{MoCl}_5$  with  $\text{H}_2$  which has been studied in some detail (Eq. 8.4). The reaction is first order in  $\text{MoCl}_5$  concentration<sup>166</sup> and 3/2 order in  $\text{H}_2$ .<sup>167</sup>



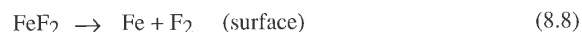
An example of the second mechanism is the reaction of  $\text{MoF}_6$  with Si substrates (Eq. 8.5).<sup>168-180</sup>



This reaction, if carried out in  $\text{H}_2$  carrier gas, can occur simultaneously with the reaction with  $\text{H}_2$  (Eq. 8.6) to give two parallel deposition mechanisms.



However, the Si reduction of  $\text{MoF}_6$  is much faster than hydrogen reduction (because  $\text{H}_2$  must first be dissociated on Mo), and so generally a Mo layer is formed by the reduction of Equation 8.5 followed by steady-state growth according to Equation 8.6. The third mechanism is shown in the reaction of  $\text{FeF}_3$  to form Fe. Macheteau<sup>192</sup> has suggested that the reaction of  $\text{FeF}_3$  occurs in the gas phase to form  $\text{FeF}_2$  (Eq. 8.7), which subsequently reacts on the surface to form high-purity Fe and  $\text{F}_2$ , (Eq. 8.8).



Other examples of this third mechanism exist. The energetics of the  $\text{FeI}_2$  system have been described.<sup>262</sup> Similarly,  $\text{AgF}$  is known to be easily defluorinated above 500 K to liberate  $\text{F}_2$  and Ag metal.<sup>263</sup> Studies of the surface chemistry of  $\text{TaF}_5$  on Si and  $\text{SiO}_2$  have shown that high-purity Ta can be formed without  $\text{H}_2$ .<sup>151</sup> Although no evidence was given, Ta deposition probably proceeds with formation of  $\text{F}_2$  (Eq. 8.9).



On silicon substrates, the CVD of metal halides can often lead to formation of metal silicides. These reactions are often the basis for selective deposition (see Ch. 9) as in the case of W (see Ch. 3) and can be used for producing metal silicides (see Ch. 1). The reactions of  $\text{TiCl}_4$  on Si surfaces have been studied in some detail and the following overall reaction pathways have been proposed (Eqs. 8.10 and 8.11).<sup>264</sup>



In the absence of  $\text{H}_2$ , excessive Si etching has been observed, as expected, based on the stoichiometry of Equation 8.10. This problem can be solved by using  $\text{TiCl}_4$  and  $\text{SiH}_4$  as source gases to produce either blanket or selective  $\text{TiSi}_2$  deposition.<sup>264</sup> Thermodynamic calculations reveal that in contrast to the facile reduction of  $\text{WF}_6$  by Si to form W at 600 K, the reduction of  $\text{TiCl}_4$  to Ti metal by Si is thermodynamically unfavorable (Eq. 8.12).<sup>265</sup>

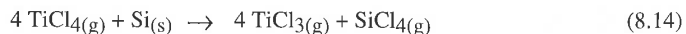


Similar calculations for the reaction of Equation 8.12 to form  $\text{TiSi}_2$  reveal it is thermodynamically favorable,  $\Delta G^{\circ}_{298} = -5.4 \text{ kcal/mol}$ . However, the reaction of Equation 8.12 is limited by three factors: (i) inhibition by the native oxide layer on Si, (ii) the relatively low thermodynamic driving force and (iii) the necessity for a supply of Si from the substrate to propagate the reaction.<sup>265</sup> Unlike  $\text{WF}_6$ ,  $\text{TiCl}_4$  does not react with  $\text{SiO}_2$  under normal CVD conditions to give Ti films.

Metal halides also exhibit other deposition mechanisms such as disproportionation. For example, the reduction of  $\text{TiCl}_4$  is further complicated by the disproportionation of sub-halides. Thermolysis of  $\text{TiCl}_4$  can result in the formation of  $\text{TiCl}_3$  and  $\text{TiCl}_2$ , observed as purple and brown deposits in CVD reactors. The  $\text{TiCl}_3$  can disproportionate to form  $\text{TiCl}_4$  and  $\text{TiCl}_2$  according to Equation 8.13.



Also, partial reduction of  $\text{TiCl}_4$  by Si is possible according to Equation 8.14. These sub-halides can then participate in other complicating reactions leading to a poorly controlled chemistry.



(8.9)

mation of metal  
Ch. 9) as in the  
see Ch. 1). The  
d the following

(8.10)

(8.11)

ed, based on the  
Cl<sub>4</sub> and SiH<sub>4</sub> as  
Thermodynamic  
form W at 600  
unfavorable (Eq.

cal/mol (8.12)

Si<sub>2</sub> reveal it is  
the reaction of  
side layer on Si,  
/ for a supply of  
4 does not react

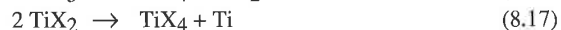
proportionation.  
oportionation of  
iCl<sub>3</sub> and TiCl<sub>2</sub>,  
disproportionate

(8.13)

.14. These sub-  
oorly controlled

(8.14)

The deposition of Ti metal from heavier halides such as TiBr<sub>4</sub> and TiI<sub>4</sub> has also been investigated. Metal was deposited on stainless steel substrates with 90% purity, and in the case of laser CVD reactions, a simple reduction to give Ti and Br<sub>2</sub> was proposed.<sup>122</sup> However, an alternative pathway is possible and involves two disproportionation steps according to reactions 8.15 through 8.17 below.



#### 8.4.2.2 Metal Alkyls

A number of metal alkyl compounds have been used as precursors for CVD experiments but often lead to the formation of metal carbides. The metals that have been examined include Sn, Pb, Zn, Cd, Ti, Cr, Zn, and W. In other cases, the metal alkyls are either not stable, not volatile, or react to give impure films.

Tin has been deposited from SnH<sub>4</sub>, Sn(CH<sub>3</sub>)<sub>4</sub>, Sn(*n*-Bu)<sub>4</sub>, and Br<sub>2</sub>Sn(*n*-Bu)<sub>2</sub>. Although not a metal alkyl compound, studies of stannane are relevant and are described here. Stannane, SnH<sub>4</sub>, has a melting point of -146 °C and a boiling point of 52.5 °C but is too unstable for most CVD applications.<sup>266-268</sup> It thermally decomposes even at 298 K to give Sn metal and H<sub>2</sub>. The thermal decomposition can be explosive under certain circumstances. The activation parameters for thermal decomposition of SnH<sub>4</sub> reveal an activation energy of 9.1 kcal/mol with rates that are first order in SnH<sub>4</sub> concentration and independent of H<sub>2</sub> pressure.<sup>269</sup> When SnD<sub>4</sub> was decomposed in the presence of H<sub>2</sub>, no HD was observed, but when a mixture of SnH<sub>4</sub> and SnD<sub>4</sub> was used, HD was found. These interpretations are consistent with a lack of chemisorption of H<sub>2</sub> on a tin surface and provide insight into the mechanism of thermal decomposition of organo-tin compounds, especially where β-hydride elimination results in formation of metal hydride intermediates.

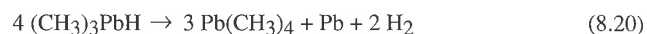
Tin(IV) compounds also undergo facile ligand redistribution reactions which can lead ultimately to the deposition of tin metal.<sup>270</sup> Analysis of the byproduct distribution of CVD of EtSnH<sub>3</sub> revealed products associated with homolytic (radical) reaction processes resulting in the well-known ligand redistribution reactions for Sn(IV).



Mechanistic studies of the thermal decomposition of organo-tin compounds during CVD experiments are not widely available, probably because Sn is primarily used as a dopant in other materials. It is possible that a β-hydride elimination mechanism is

operative (where  $\beta$ -hydrogen atoms are available) analogous to the case of Al, but the homogeneous solution chemistry of tin(IV) alkyls is dominated by radical mechanisms. Thermal decomposition of  $\text{Ph}_3\text{SnH}$  in the gas phase reveals products consisting of a small amount of benzene,  $\text{SnPh}_4$ ,  $\text{Sn}_2\text{Ph}_6$ , and Sn that are consistent with homolytic processes.<sup>271</sup>

Lead, zinc, and cadmium have been primarily used as dopants in other materials; therefore, the thermal decomposition of these metal alkyls in the absence of other species has not been studied in detail. Lead(IV) alkyl compounds probably undergo thermal decomposition by homolytic mechanisms analogous to the photochemically-induced reactions.<sup>246</sup> Alkyl lead hydrides,  $\text{R}_{(4-n)}\text{PbH}_n$ , undergo thermal and photochemical decomposition below room temperature in the liquid phase by various routes such as those shown in Equation 8.20.<sup>272-274</sup> Similar mechanisms may occur in CVD processes.



Zinc and cadmium alkyl compounds also appear to thermally decompose via metal-carbon bond homolysis, although much more attention has been devoted to studies of their photochemically-induced decomposition. The typical temperature for the complete decomposition of  $\text{Cd}(\text{CH}_3)_2$  in  $\text{H}_2$  is  $\sim 380^\circ\text{C}$ .<sup>275</sup> A study of the adsorption behavior of  $\text{Zn}(\text{CH}_3)_2$  and  $\text{ZnEt}_2$  on Si(100) surfaces revealed that these species dissociated below 300 K to produce alkyl species and zinc metal.<sup>228</sup> At higher temperatures (400-600 K), Zn desorbed and left the alkyl species on the surface. Dimethyl zinc resulted in formation of surface  $\text{CH}_3$  groups which either desorbed as  $\text{CH}_3\cdot$  at 825 K or were dehydrogenated to form  $\text{CH}_x$ , C, and  $\text{H}_2$ . Further reaction of these species resulted in formation of acetylene,  $\text{H}_2$ , and SiC. Diethyl zinc decomposed to give surface Et $\cdot$  groups which underwent  $\beta$ -hydride elimination to give both gas-phase and surface ethylene. The physisorbed ethylene either desorbed at 650 K or decomposed to  $\text{CH}_x$ , C, and  $\text{H}_2$ .

Chemical vapor deposition experiments using  $\text{Ti}(\text{CH}_2\text{-}t\text{-Bu})_4$  resulted in formation of TiC rather than Ti metal at a substrate temperature as low as  $150^\circ\text{C}$ .<sup>76</sup> Even in the presence of a hydrogen pressure of  $10^{-2}$  torr, TiC was formed. The films were amorphous as deposited and crystallized only on heating above  $1100^\circ\text{C}$ . Mechanistic studies revealed a reaction pathway that involved  $\alpha$ -hydrogen abstraction to form neopentane and a titanium alkylidene intermediate.

Similar observations were made with  $\text{Cr}(\text{CH}_2\text{-}t\text{-Bu})_4$  and  $\text{Cr}(\text{N-}i\text{-Pr})_3$  which gave amorphous films with Cr:C ratios of 1.4:1 and 1.9:1 as deposited at  $330^\circ\text{C}$ .<sup>158</sup> On annealing at  $600^\circ\text{C}$  for 18 hours under vacuum ( $10^{-3}$  torr), crystalline  $\text{Cr}_3\text{C}_2$  was formed. A byproduct analysis of CVD using  $\text{Cr}(\text{CH}_2\text{-}t\text{-Bu})_4$  revealed the presence of neopentane, isobutylene, propene, and tetramethylhexene.<sup>158</sup> A mechanism analogous to that proposed for the thermal decomposition of  $\text{Ti}(\text{CH}_2\text{-}t\text{-Bu})_4$  was implicated, although binuclear processes were not ruled out.<sup>276</sup> Similar results were observed for other early transition metal alkyl compounds including  $\text{Zr}(\text{CH}_2\text{-}t\text{-Bu})_4$  which forms ZrC and  $(t\text{-Bu-CH}_2)_3\text{W}\equiv\text{CSi}(\text{CH}_3)_3$  which forms WC.<sup>277</sup>



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### 8.4.2.3 Complexes with Unsaturated Organic Ligands: Alkenes, Alkynes, Alkyls, Metallocenes, and Related Complexes

**Alkene and alkyne complexes:** Alkene and alkyne  $\pi$ -complexes of metals have been investigated mainly for the cases of Ir, Ru, and Rh. In general, better results have been obtained in the presence of hydrogen in which case hydrogenation of the unsaturated organic ligand could occur. Few generalizations can be made about reaction pathways because of the wide variety of precursors that have been examined.

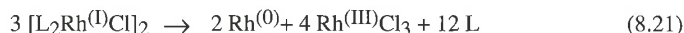
The reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{1,5-COD})$  and  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Ir}(\text{1,5-COD})$  in hydrogen and low O<sub>2</sub> partial pressure led to formation of high-purity (<1% C) Ir films at 120 °C.<sup>215</sup> However, when the deposition was carried out in vacuo, 80% C was incorporated. Under an H<sub>2</sub> atmosphere, byproduct analysis revealed the presence of only saturated hydrocarbons, cyclooctane, and presumably methylcyclopentane, although this was not stated clearly. The analysis suggested a simple mechanism in which the organic ligands were hydrogenated to form stable volatile species which desorbed from the surface. The volatile byproducts were not collected in the deposition experiment under an O<sub>2</sub> atmosphere, and the lack of oxidation of the film was consistent with the low oxophilicity of Ir suggesting a mechanism in which the organic substances were oxidized to form volatile species which desorbed from the surface.

The compound  $[(\text{1,5-COD})\text{Ir}(\mu\text{-OAc})]_2$  is thermally unstable and decomposed in the precursor reservoir during CVD experiments in vacuo.<sup>215</sup> Proton NMR spectroscopy revealed the presence of cyclooctadiene, cyclooctene, and cyclooctane in approximately equal amounts and suggested the alkene portion of the precursor was hydrogenated. Thermogravimetric analysis with mass spectroscopy also revealed the presence of CO<sub>2</sub> and ethane, thought to arise from thermal decomposition of the acetate ligands. This suggests a rather complicated reaction mechanism in which ligand hydrogenation and decomposition both occur where the presence of H<sub>2</sub> or O<sub>2</sub> could drastically change the reaction pathways. In other work, the thermal decomposition of  $(\text{1,5-COD})\text{Rh}(\text{OR})$  compounds produced 1,5-cyclooctadiene, 1,3-cyclooctadiene, and cyclooctane analogous to the observations for the carboxylate complexes.<sup>278</sup>

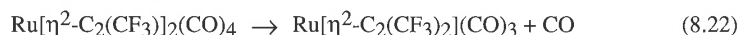
Thermal laser-assisted CVD of  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^2\text{-C}_2\text{H}_4)_2$  (M = Rh and Ir) revealed some insight into thermal CVD processes.<sup>207</sup> Laser-assisted CVD of these compounds under H<sub>2</sub> resulted in formation of pure Rh and Ir films when the substrate was irradiated in the presence of the precursor for 20 min and then the deposit was further irradiated under H<sub>2</sub> for 20 min in the absence of the precursor. Irradiation of the substrate under H<sub>2</sub> for 20 min without a subsequent annealing step and in the absence of the precursor resulted in deposits that analyzed as C:Rh = 5:1. Therefore, the authors proposed that irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)$  resulted in loss of the ethylene ligands, probably in the gas phase, with formation of " $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)$ ." Subsequent annealing with hydrogen resulted in reduction of Rh<sup>I</sup> to Rh<sup>0</sup> with loss of the hydrogenated cyclopentadienyl ligand. However, under the conditions used, laser-assisted gas-phase reactions seem unlikely

because of the small deposit dimensions and low pressures involved, and loss of the neutral ligand may have occurred during precursor adsorption and reaction.

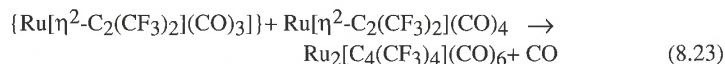
In other work, the lability of a series of  $\text{Rh}^{\text{I}}$  compounds  $(\text{L}_2\text{RhCl})_2$  [where  $\text{L}_2 = 1,5\text{-COD}$ , NBD (norbornadiene) and  $(\eta^2\text{-C}_2\text{H}_4)_2$ ] was studied with respect to formation of Rh under air, nitrogen, and 7%  $\text{H}_2$  in  $\text{N}_2$  atmospheres.<sup>278</sup> The results revealed that the thermal decomposition behavior depended on the nature of the alkene ligand and the composition of the atmosphere. Under 7%  $\text{H}_2$  in  $\text{N}_2$  atmosphere, the onset of thermal decomposition of these species occurred in the following order:  $\text{L}_2 = (\eta^2\text{-C}_2\text{H}_4)_2$ , 91 °C; NBD, 143 °C; 1,5-COD, 212 °C. Under a nitrogen atmosphere,  $(\text{L}_2\text{RhCl})_2$ , [ $\text{L}_2 = \text{NBD}$  and  $(\eta^2\text{-C}_2\text{H}_4)_2$ ], underwent weight loss consistent with loss of one or more alkene ligands followed by formation of Rh metal at higher temperatures. In contrast,  $[(1,5\text{-COD})\text{RhCl}]_2$  formed Rh metal directly. In air, thermal decomposition generally resulted in formation of crystalline Rh metal followed by oxidation above 500 °C to form crystalline  $\text{Rh}_2\text{O}_3$ , except for  $[(\eta^2\text{-C}_2\text{H}_4)_2\text{RhCl}]_2$ , which gave  $\text{Rh}_2\text{O}_3$  directly. The weight loss corresponding to formation of "RhCl" by loss of the neutral ligand was a common feature of these reactions. However, X-ray diffraction studies showed that "RhCl" contained a significant amount of crystalline Rh and was more likely to be the disproportionation products Rh and  $\text{RhCl}_3$ , formed according to Equation 8.21. These results imply that while a reducing ambient is desirable to facilitate the reduction of the metal, complexes of noble metals can be thermally reduced in air to form the corresponding crystalline metal.



High-purity Ru films were deposited at 500 °C on Si substrates from the ruthenium alkyne complex  $\text{Ru}(\text{CO})_4[\eta^2\text{-C}_2(\text{CF}_3)_2]$  under dynamic vacuum.<sup>198</sup> At lower substrate temperature (300 °C), the thickness of the film was noticeably diminished and a yellow crystalline solid was observed. At a substrate temperature of 150 °C, the yellow crystalline solid was formed in sufficient quantity that it could be isolated and characterized as the dimer  $\text{Ru}_2[\text{C}_4(\text{CF}_3)_4](\text{CO})_6$ , which was also obtained in homogeneous solution on refluxing the starting material in toluene. As a result of this observation, Senzaki et al.<sup>198</sup> proposed that the first step in thermal decomposition of  $\text{Ru}(\text{CO})_4[\eta^2\text{-C}_2(\text{CF}_3)_2]$  was carbonyl dissociation in the gas phase (Eq. 8.22).



This product may then react with the starting material to form the dimer according to Equation 8.23.





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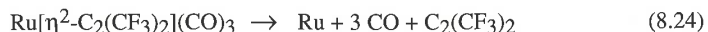
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However, at higher temperatures thermal decomposition of the tricarbonyl intermediate may dominate resulting in Ru deposition (Eq. 8.24).



These byproducts were identified by trapping the volatile decomposition product and analyzing by  $^{19}F$  NMR spectroscopy and GC-MS-FTIR. Evidence for the species  $C_4F_{14}$  and  $C_4F_{12}$  was obtained. In addition,  $Ru_2[C_4(CF_3)]_4(CO)_6$  also thermally decomposed to give Ru films. However, whether or not the dimeric species is formed as an intermediate during decomposition was not clear.

**Allyls:** The allyl ( $C_3H_5$  or propenyl) complexes of Ir and Rh provide routes to the pure metals under certain conditions. The reactions of  $Rh(\eta^3\text{-allyl})_3$  on  $TiO_2$  surfaces have been investigated under UHV conditions.<sup>74,209</sup>  $Tri(\eta^3\text{-allyl})rhodium$  reacted with OH groups on the surface to form a diallylrhodium species. Upon reaction with hydrogen at 60-100 °C, an allylrhodium hydride was formed. Further reaction with hydrogen at 120-150 °C resulted in formation of  $TiO_2\text{-RhH}_2$  which reductively eliminated  $H_2$  above 400 °C to yield Rh metal. No direct analysis of reaction products was reported; however, these results suggest that the purity of films can be increased by the presence of hydrogen.

In a comparison of the CVD of  $M(\eta^3\text{-allyl})_3$  ( $M = Rh$  and  $Ir$ ) in vacuo, under  $H_2$ , and in the presence of  $H\cdot$ , the metal films were contaminated with C to approximately the same extent in vacuo and under  $H_2$  (13-17 at.% C).<sup>74</sup> However, introduction of atomic hydrogen increased the purity (2 at.% C) of Ir and Rh films deposited in plasma-assisted experiments. It was proposed that the atomic  $H\cdot$  aids cleavage of the M-allyl bonds with formation of propene and propane. Any carbon incorporated during deposition is then preferentially etched from the growing film by the plasma.<sup>74</sup>

A detailed study of the thermal decomposition pathway of  $M(\eta^3\text{-allyl})_4$  ( $M = Mo$  and  $W$ ) has been carried out in both a partial pressure of  $H_2$  and under vacuum.<sup>75</sup> The volatile byproducts were trapped and analyzed by  $^1H$  NMR spectroscopy. The films deposited from these precursors consisted primarily of the carbides, MC, together with graphitic carbon as determined by XPS, when the deposition was carried out under vacuum. Formation of unidentified metal oxides (due to failure to scrub the  $H_2$  carrier gas) was observed under  $H_2$ . The major volatile byproducts (>95%) identified by  $^1H$  NMR spectroscopy were propene and propane. Minor amounts of benzene, ethylene, and ethane were also observed. No evidence for hexadiene was found, in contrast to the CVD of  $Pd(\eta^3\text{-allyl})_2$  where the product distribution was 67% propene and 33% hexadiene,<sup>76</sup>  $Te(\eta^1\text{-allyl})_2$  where hexadiene was exclusively observed,<sup>175</sup> and  $Se(\eta^1\text{-allyl})_2$ <sup>279</sup> where a 2 : 1 ratio of propene to hexadiene was observed. The absence of hexadiene in the case of  $M(\eta^3\text{-allyl})_4$  suggests homolytic bond dissociation processes did not occur. A  $\beta$ -hydride elimination mechanism would favor formation of allene or propyne as observed for  $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Ta}(\eta^3\text{-allyl})$  in solution. Reaction pathways involving either  $\alpha$ -

hydride elimination or vinyl C-H activation are proposed to be more reasonable for the Mo and W species. These accounted for the observed decomposition products and the resulting increase in the M-C bond order of the intermediate which would favor metal carbide formation. These experiments show the poor characteristics of early transition metal allyl complexes for deposition of pure metal films.

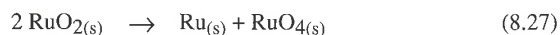
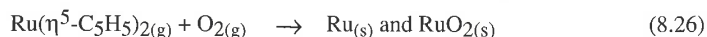
**Metallocenes and Related Complexes:** Metallocenes,  $M(\eta^5\text{-C}_5\text{H}_5)_2$ , used in conjunction with  $\text{H}_2$  often allow deposition of pure metals. The metallocenes that have been studied in most detail include those of Fe, Cr, Ru, Co, Mo, Ni, and Nb. However, the deposition temperatures tend to be high, often over  $500^\circ\text{C}$ . A patent has discussed CVD using Mn, Ti, Mg, and V cyclopentadienyls at temperatures of 500 to  $800^\circ\text{C}$ .<sup>280</sup> Two classes of reaction pathways are found, one in which the  $\text{C}_5\text{H}_5^-$  ligand reacts to form various volatile and involatile species and one in which it reacts with hydrogen to give  $\text{C}_5\text{H}_6$ . A problem with the use of many metallocene precursors is that the dissociation of the organic portion of the precursor on the metal surface frequently leads to significant C incorporation. For example, CVD using  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$  and  $\text{Cr}(\text{cumene})_2$  leads to formation of Cr and  $\text{Cr}_3\text{C}_2$ .<sup>77,159</sup> Similarly, CVD using  $\text{Ti}(\eta^6\text{-C}_6\text{H}_6)_2$  leads to  $\text{TiC}$ .<sup>280</sup>

Although CVD using  $M(\eta^5\text{-C}_5\text{H}_5)_2$  has been studied extensively, detailed studies of mechanistic aspects are quite limited. In the absence of hydrogen the initial product  $\text{C}_5\text{H}_5^\bullet$  can react to form dihydrofulvalene or disproportionate heterogeneously to incorporate C in the growing film. Under  $\text{H}_2$ , the reaction of Equation 8.25 has been proposed.<sup>31</sup>



This idea is supported by results in which  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  gives pure Fe at temperatures ranging from  $400$  to  $900^\circ\text{C}$ , and  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$  deposits pure Co between  $300$  and  $700^\circ\text{C}$ . However,  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2$  cannot be used under these conditions due to reaction with  $\text{H}_2$  at the transport temperature.

Chemical vapor deposition using  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$  has been studied in some detail. In the presence of oxygen, reaction of  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$  leads to formation of Ru and  $\text{RuO}_2$  (Eq. 8.26), which can be converted to  $\text{RuO}_4$  (Eq. 8.27). This latter species can desorb at higher temperatures (near  $900^\circ\text{C}$ ) (Eq. 8.28) to provide the pure metal.<sup>35</sup> However, this approach is necessarily a high-temperature approach which is incompatible with many substrates.



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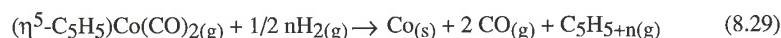
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The reactivity of other unsaturated  $\pi$ -complexes of metals was investigated for Cr, Mo, and Co. The case of  $(\eta^6\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$  ( $\text{C}_7\text{H}_8$  = cycloheptatriene) was investigated in detail<sup>157</sup> and resulted in formation of Cr with high levels of C and small amounts of O. Analysis of the products showed formation of  $\text{C}_7\text{H}_8$  (unchanged),  $\text{C}_6\text{H}_6$  (loss of  $\text{CH}_2$ ), cycloheptadiene (reaction with  $\text{H}_2$ ), toluene (rearrangement), and styrene (addition of C). Labelling studies with  $^{13}\text{CO}$  showed that the majority of the carbon in the films derived from the  $\text{C}_7\text{H}_8$ . The cleavage of the  $\text{C}_7\text{H}_8$  was proposed as the mechanism for carbon incorporation. This study shows the complex reaction chemistry that is possible in some cases.

The reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  in hydrogen and helium have been studied, and deposition was observed between 300 and 600 °C. Films without hydrogen contained equal amounts of carbon and cobalt while films deposited in hydrogen had far lower levels of carbon.<sup>201</sup> Although the byproduct distribution was not studied, Equation 8.29 was proposed to account for the deposition of pure Co under  $\text{H}_2$ . This equation again relies on hydrogenation of the organic ligand to form a stable, volatile reaction product.



Chemical vapor deposition of  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$  leads to formation of involatile products and cyclopentadiene, dicyclopentadiene, and cyclopentene suggesting that protonation and  $(\eta^5\text{-C}_5\text{H}_5)\text{-Cr}$  bond homolysis also occurred.<sup>158</sup> It was suggested that the carbon was derived from the  $\text{C}_5\text{H}_5^-$  ring and not from the CO based on the results of Truex<sup>157</sup> for  $(\eta^6\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$ .

#### 8.4.2.4 Metal Carbonyls

Metal carbonyl complexes have been studied extensively as precursors for CVD of Co, Fe, Mo, and Cr. In the cases of Co and Fe, high-purity deposits can be obtained. In contrast, most other metal carbonyls produce films that are contaminated with metal carbides, metal oxides, and graphitic carbon. The reason for this is that CO is dissociatively adsorbed on most metal surfaces and as a result C and O are incorporated into the film.

The most well-studied system is  $\text{Fe}(\text{CO})_5$ . Ultra-high vacuum studies have shown that reaction on the first monolayer involves dissociation of the CO to form an oxygen overlayer. After the formation of this overlayer, dissociation of the CO no longer occurs and the reaction proceeds by Equation 8.30.

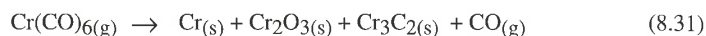


Adsorbing and dissociating  $\text{Fe}(\text{CO})_5$  molecules displace the oxygen overlayer as deposition continues. Thus, the only carbon impurities in the film are found at the interface with the substrate.<sup>194</sup>

Zaera has also studied the surface chemistry of iron pentacarbonyl using TPD and XPS.<sup>281</sup> Desorption was molecular and took place in two stages. Most of the adsorbate desorbed near 180-195 K. A small fraction of the adsorbed precursor decomposed as was shown by XPS. The fragmentation took place between 170 and 240 K and resulted in Fe and chemisorbed CO. However, high-purity films could be grown at steady state conditions because the incoming reactant displaced CO from the surface; these results agree with those above.<sup>194</sup> Similar results were obtained by Jackman and Foord<sup>282</sup> who also studied the UV photolysis of adsorbed iron pentacarbonyl under UHV conditions.

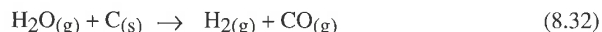
Syrkin and Kir'yanov studied the thermodynamics of iron CVD using  $\text{Fe}(\text{CO})_5$ .<sup>283</sup> Analysis of phase diagrams suggested that only Fe,  $\text{Fe}_3\text{C}$ , and  $\text{Fe}_3\text{O}_4$  can exist at temperatures between 200 and 300 °C. They concluded that small amounts of  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{O}_4$  could be formed during CVD due to the reaction of Fe with CO.

Reactions of many metal carbonyls lead to formation of metal carbides due to the catalytic dissociation of CO on the metal. One example is the reaction of  $\text{Cr}(\text{CO})_6$  (Eq. 8.31).<sup>81</sup>

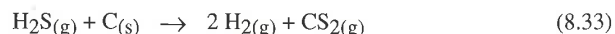


These results suggest that metal carbonyls are good choices as precursors only for those elements which do not allow surface dissociation of CO. In cases where dissociation occurs, it may be possible to remove some of the carbon and oxygen impurities by reaction with added reagents.

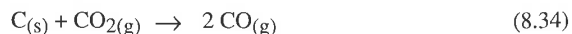
The reactions of  $\text{Mo}(\text{CO})_6$  have been studied in some detail and provide an example where film purity can be increased by creating additional reaction pathways.<sup>173</sup> In certain temperature ranges, the dissociation of CO can be minimized to provide relatively pure Mo. Various strategies for removal of C from the surface were devised to improve the film purity over a wider temperature range. One approach is to add water which can react with carbon in various forms to form hydrogen and CO which then desorb from the surface during film growth (Eq. 8.32).



However, the addition of water can also lead to formation of  $\text{MoO}_3$ , so this approach has limited utility. Similarly, addition of  $\text{H}_2\text{S}$  can increase film purity (Eq. 8.33), but again only under certain conditions.



Another approach is to introduce  $\text{CO}_2$  which oxidizes C to CO (Eq. 8.34).



Again, this approach was only useful for certain conditions, especially since reaction 8.34 regenerates CO which was responsible for the impurity incorporation in the first place. An analogous approach for removing impurities from surfaces during film growth has been used for tungsten CVD from organometallic precursors (see Ch. 3).

#### 8.4.2.5 Trifluorophosphines

Complexes with  $\text{PF}_3$  have been used to deposit metal films at temperatures between 200 and 300 °C. Related complexes include the phosphine complexes of Cu(I) compounds.<sup>85-87</sup> The trifluorophosphine complexes of Cr, Mo, Fe, Ru, Co, Rh, and Ir are volatile and suitable for CVD. However, few results are available in the literature for these precursors. A likely reaction pathway for some metals is the reaction of the precursor to give the metal and adsorbed  $\text{PF}_3$ . The  $\text{PF}_3$  can desorb from the surfaces of many metals. For example (see Ch. 5),  $\text{P}(\text{CH}_3)_3$  cleanly desorbs from copper surfaces to give high-purity copper when precursors incorporating  $\text{PR}_3$  ligands are utilized.

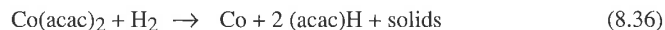
The reactions of  $[(\text{PF}_3)_2\text{RhCl}]_2$  have been investigated in some detail.<sup>208</sup> Trapping of reaction products showed formation of  $\text{PF}_3$  as the only volatile product. No fluorine was found in the films by XPS and XRD. The films did, however, contain chlorine. X-ray photoelectron spectroscopy also revealed the presence of rhodium in both reduced ( $\text{Rh}^0$ ) and oxidized ( $\text{Rh}^{\text{III}}$ ) states. Crystalline Rh was identified by X-ray powder diffraction. As a result of these observations, the authors suggested that the  $\text{PF}_3$  ligand desorbed intact from the surface after reaction of  $[(\text{PF}_3)_2\text{RhCl}]_2$  leading to formation of Rh and  $\text{RhCl}_3$  according to the disproportionation reaction of Eq. (8.35).<sup>208</sup>



#### 8.4.2.6 Metal $\beta$ -diketonates

Many metal  $\beta$ -diketonates in the presence of hydrogen allow deposition of high-purity metal. This is similar to the situation for CVD of copper from  $\text{Cu}(\beta\text{-diketonate})_2$  species (Chs. 4 and 5). The major disadvantages are that in some cases the deposition temperature is high and the vapor pressures are relatively low leading to low deposition rates. The metals Co, Cr, Fe, Rh, and Ru have been studied in most detail; however, only a few studies of the reaction byproducts have been reported. More details of the decomposition mechanisms of  $\beta$ -diketonate ligands have recently been obtained from UHV studies of Cu(I) and Cu(II)  $\beta$ -diketonate compounds (see Chs. 4 and 5). These studies suggest that the two major reaction pathways are formation of the  $\beta$ -diketone via reaction with  $\text{H}_2$  and decomposition of the  $\beta$ -diketonate ligand to form a variety of products. The latter is undesirable because it can lead to impurities. An example of these two reaction pathways is CVD using  $\text{Co}(\text{acac})_2$ . No deposition was observed in the absence of hydrogen. In the presence of hydrogen, both  $(\text{acac})\text{H}$  and other less volatile species were formed (Eq. 8.36).<sup>100</sup>

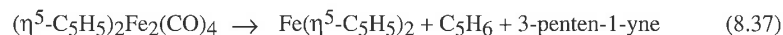




These species were probably formed by the catalytic reactions of the acac ligand on the Co surface (Eq. 8.36).

#### 8.4.2.7 Bi- and Multi-Nuclear Complexes

Several bi- and multi-nuclear complexes have been used for CVD of Mn, Fe, and Co. These complexes include metal carbonyls such as  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Co}_2(\text{CO})_8$  and more complex species such as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$  and  $\text{Rh}_2(\text{Cl})_2(\text{CO})_4$ . However, in only a few cases have the reaction products been examined. The reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$  leads to formation of several products (Equation 8.37).<sup>196</sup>



The 3-penten-1-yne was proposed to be derived from a ring opening reaction of the  $(\text{C}_5\text{H}_5)^-$  ligand. This ligand decomposition can lead to carbon contamination as observed in other cases such as copper deposition from  $(\eta^5\text{-C}_5\text{H}_5)\text{CuL}$  complexes (see Ch. 5).

#### 8.4.2.8 Heteronuclear Complexes

Heteronuclear complexes have been used to deposit films containing numerous metals. One of the main motivations for understanding the reaction pathways is to develop strategies to allow deposition of films with controlled stoichiometry. This requires that after adsorption and reaction of the precursor, both of the desired elements are retained in the film even if two species are formed, each containing one of the metals found in the precursor. Therefore, it is desirable to find reaction pathways that do not result in formation of volatile metal-containing intermediates or that give intermediates that, if formed, react rapidly to give pure metal. Only in a few cases has enough information been obtained to answer these questions.

The reaction of  $(\text{CO})_4\text{CoGaCl}_2(\text{THF})$  in hydrogen led to formation of CoGa,  $\text{CH}_4$ , THF, CO, acetone, and HCl.<sup>48</sup> The CO and acetone are presumably formed from THF decomposition on the surface or from the carbonyl. The films had 3% C at 450 °C with lower C content at lower temperatures but with correspondingly higher O content. Deposition in inert gas gave much higher carbon content.<sup>48</sup> The precursor stoichiometry could be retained in the film.

Films of Fe-Co and Fe-Ni deposited using  $(\eta^5\text{-C}_5\text{H}_5)\text{FeCo}(\text{CO})_6$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}_2\text{Co}(\text{CO})_9$ ,  $\text{HFeCo}_3(\text{CO})_{12}$ , and  $(\eta^5\text{-C}_5\text{H}_5)\text{FeNi}(\text{CO})_3$  contained roughly 4 to 8% C and O.<sup>251,254</sup> Addition of oxygen during deposition resulted in formation of the metal oxides. The C and O contamination was presumably derived from both the  $(\text{C}_5\text{H}_5)^-$  and CO ligands, although no evidence was given. Again, the same stoichiometry was found in both the precursor and film.

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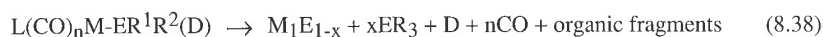
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Reaction of  $H_3SiCo(CO)_4$  led to the formation of  $H_2$ ,  $CO$ ,  $SiH_4$ , and  $CH_4$ , which suggests the stoichiometry was not preserved. The  $CH_4$  was proposed to derive from the reaction of  $CO$  with  $H_2$ .<sup>253</sup> Stauff et al. studied the deposition of  $Mn_2Si$  from  $Mn_2(CO)_{10}(\mu-SiH_2)$ .<sup>258</sup> This same stoichiometry was preserved in the film. However, high levels of O and C were observed in films deposited at all temperatures from 300 to 500 °C. The source of the C was thought to be the carbonyl groups which did not fully desorb from the surface.

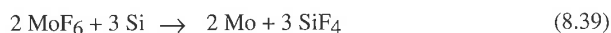
The reactions of  $L(CO)_nM-ER^1R^2(D)$  (see Table 8-21) have been examined via film characterization and volatile byproduct analysis.<sup>259</sup> The following reaction was proposed:



where the terms are defined in Table 8-21. In many cases, the metal ratio of the precursor was not necessarily reproduced in the films. For example, during reaction of  $(CO)_4CoGa[CH_2Si(CH_3)_3]_2(THF)$ , the formation of  $Ga[CH_2Si(CH_3)_3]_3$  was observed. It was suggested that the stoichiometry could be maintained if the formation of group 13 alkyls is much slower than fragmentation to give involatile intermediates which react to form the metal. In general, complex chemistry was observed for the many systems that were studied.

### 8.4.3 Selectivity

The selectivity for deposition onto one type of surface in the presence of another has not been studied for the metals discussed in this chapter except in a few cases. A review by Carlsson discusses selective CVD of metals including Mo on patterned substrates.<sup>284</sup> In the presence of  $SiO_2$ ,  $MoF_6$  can provide selective deposition on Si.<sup>166-170</sup> Selectivity is obtained because the  $MoF_6$  cannot react with  $SiO_2$  while Si can reduce the Mo as shown by Equation 8.39.



The selectivity of  $Co(\eta^5-C_5H_5)_2$  has been studied for  $Si/SiO_2$ .<sup>31,201</sup> Dicyclopentadienylcobalt is selective for  $SiO_2$  and does not deposit on Si when hydrogen is present. In the absence of hydrogen, no deposition takes place on  $SiO_2$  or Si up to 900 °C. Similarly,  $Fe(\eta^5-C_5H_5)_2$  deposits on  $SiO_2$  and not on Si when deposition is carried out in hydrogen.<sup>31,201</sup> Again, no deposition was observed on either  $SiO_2$  or Si in the absence of hydrogen. In contrast,  $Co_2(CO)_8$  was not selective for Si, reacted on both  $SiO_2$  and Si, and behaved similarly in both He and  $H_2$ .

Tantalum pentachloride is not selective for Si in the presence of SiO<sub>2</sub> in contrast to MoF<sub>6</sub> and WF<sub>6</sub> (see Ch. 3).<sup>151</sup> However, UHV studies have shown that TaCl<sub>5</sub> is a good precursor for blanket deposition of Ta.<sup>151</sup>

In general, few studies have addressed selective CVD using the precursors considered in this chapter. It is likely, however, that many of these precursors would exhibit selectivity if reacted under appropriate conditions and that the surface modification techniques discussed in Chapters 5 and 9 would allow some tailoring of the selectivity. General principles of selective CVD are discussed in Chapter 9.

## 8.5 Summary and Conclusions

Chemical vapor deposition of the metals discussed in this chapter (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Zn, Cd, Sn, and Pb) has been studied to a much lesser extent than CVD of metals such as W, Al, Cu, Au, Ag, Pt, Pd, and Ni. However, several general statements can be made.

- The metal halides, carbonyls, and cyclopentadienyls have been studied most extensively. (Relatively few organometallic precursors have been examined.)
- The major classes of metal-organic and organometallic precursors that have been studied are carbonyls, alkenes, alkynes, allyls, cyclopentadienyls, arenes, and  $\beta$ -diketonates.
- For most of the metals, low-temperature CVD of high-purity metal has not yet been demonstrated. This is a particularly important issue for metals such as Ti which have applications in the microelectronics industry.
- Little is known about the reaction pathways and kinetics of CVD of the metals discussed in this chapter except for Co, Mo, Ta, Cr, and Fe.
- Other than selective Mo CVD which has been examined in detail, there have been only a few studies of the selective deposition onto one type of surface in the presence of another.
- Heteronuclear single-source precursors have only been investigated in a few cases. These precursors may provide alternative routes to more complex materials such as silicides, germanides, and alloy phases and may also allow better control of compositional homogeneity, stoichiometry, and phase purity. However, the benefits have not yet been clearly demonstrated. These precursors have the disadvantage of relatively low vapor pressure, although this problem can be overcome by using alternative precursor delivery methods (see Ch. 9).
- Hydrogen may be added to improve the purity of films produced with precursors containing halide, cyclopentadienyl,  $\beta$ -diketonate, allyl, alkene, and alkyne ligands.



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- The addition of oxygen improves film purity in cases where the metal does not form a stable oxide. The oxygen allows oxidation of organic species to form volatile products.

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