

LOW TEMPERATURE MOCVD ROUTES TO THIN FILMS FROM TRANSITION METAL PRECURSORS

GREGORY S. GIROLAMI* AND JOHN E. GOZUM

School of Chemical Sciences and Materials Research Laboratory,
The University of Illinois at Urbana-Champaign, Urbana, IL 61801

ABSTRACT

A review is presented of early and recent advances in the metal-organic chemical vapor deposition (MOCVD) of thin films from organotransition metal and related precursors. Routes to pure metals and alloys, metal carbides, metal borides, metal nitrides, metal silicides, and related materials will be summarized. Also included is a discussion of both the advantages and disadvantages of employing metal-organic precursors that contain transition elements.

INTRODUCTION

The synthesis of inorganic materials has often (and traditionally) involved the use of high temperatures. During the past few decades, there has been increasing interest in synthetic procedures that can generate useful inorganic solids under relatively mild conditions; two specific examples are the sol-gel preparation of silicate glasses from the hydrolysis of silicon alcoxides, and the chemical vapor deposition of GaAs from trimethylgallium and arsine. In this paper, we will review recent developments in the low-temperature chemical vapor deposition of thin films that contain transition metals from metal-organic precursors.

The deposition of films that contain transition metals is usually accomplished by reduction of a transition metal halide precursor such as $TiCl_4$ or WF_6 with hydrogen [1-7]. In the absence of other components in the gas stream, deposition of a pure metal film usually results. However, by adding to the gas stream a volatile heteroatom source such as methane, boron trichloride, or silane, the corresponding carbide, boride, silicide, etc, can be obtained. Generally, the deposition of thin films from a transition metal halide precursor does not occur unless the temperature is relatively high (often above about 800°C), largely because the metal-chlorine bonds are strong and transition metal halides are quite thermally robust species. In some cases, the minimum deposition temperature can be lowered somewhat by employing plasma- or laser-enhancement techniques.

There are several reasons to develop metal-organic precursors as alternatives for the deposition of thin films that contain transition metals, despite the demonstrated utility of transition metal halides as CVD sources. First, the halides of many of the transition elements, such as Pd and Mn, are not particularly volatile and are thus unsuited as CVD precursors. Second, in many CVD processes the presence of a halogen is detrimental since it can promote corrosion of the film either during deposition or, if halogen atoms become incorporated into the film, after deposition by exposure of the finished product to air and water. Third, there are good reasons to expect that

suitably designed metal-organic precursors will allow thin films that contain transition metals to be deposited at lower temperatures. Lowering the temperature at which solid materials can be synthesized not only increases energy efficiency but also makes it possible to use the material in applications where higher temperatures lead to undesirable consequences. Some of the consequences of high temperature synthetic methods can be very difficult to circumvent, such as interlayer atomic diffusion, decohesion of overlayers due to mismatches in thermal expansion coefficients, or temperature-induced changes in the shape or the crystallinity of the substrate or nearby structures. Potentially, all of these undesirable phenomena can be avoided by employing suitably tailored transition metal-organic precursors that undergo deposition at lower temperatures.

The next few sections briefly review recent investigations of transition metal-organic compounds as CVD precursors. This review is not intended to be comprehensive, but rather serves as a guide to the literature.

ROUTES TO PURE METALS AND ALLOYS

Carbonyls. The year 1990 marks the 100th anniversary of the earliest use of an organotransition metal compound as a CVD precursor. In 1890, Ludwig Mond announced the discovery of the first binary metal carbonyl, nickel tetracarbonyl, and showed that this volatile compound deposits nickel metal with release of the carbon monoxide ligands at 230°C [8-10]. Mond started the Mond Nickel Company at the turn of the century to manufacture high-purity nickel by MOCVD from $\text{Ni}(\text{CO})_4$, and this process is still used today on a large scale (over 10,000 tons/year).

In the first half of this century, new binary metal carbonyls of most of the transition elements were discovered, and each in turn was explored as a potential CVD precursor. Although $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$ give reasonably pure iron [11-13] and cobalt [14, 15] metal at 200°C, other metal carbonyls such as chromium, molybdenum, or tungsten hexacarbonyl generally deposit films that contain mixtures of the pure metal, the metal oxide, the metal carbide, and graphitic carbon [16-27]. This is quite understandable, since carbon monoxide readily chemisorbs on most metal surfaces to give surface-bound oxygen and carbon atoms, which under CVD conditions become incorporated into the growing film. In contrast, the successful deposition of Ni, Fe, and Co from their corresponding carbonyls is possible since carbon monoxide does not dissociate as readily on these metals [28, 29].

An interesting new approach is the use of metal carbonyl [30] and mixed-metal carbonyl clusters [31, 32] as CVD precursors. A carbon monoxide stream that contains the cluster $\text{FeCo}_3\text{H}(\text{CO})_{12}$ deposits an iron/cobalt alloy of stoichiometry Fe_2Co at 300-350°C. This change in the Fe:Co ratio was attributed to disproportionation of the cluster upon heating to form $\text{Fe}(\text{CO})_5$ and involatile $\text{Co}_4(\text{CO})_{12}$, which does not transport to the hot zone. The mixed metal dimer $\text{CpFeCo}(\text{CO})_6$ was also investigated [31].

Metallocenes. Bis(cyclopentadienyl)metal compounds, the metallocenes, have been explored as potential CVD precursors

since the 1960's. A patent on the use of vanadocene, chromocene, manganocene, ferrocene, cobaltocene, and nickelocene reports that pure metal films can be obtained by CVD at temperatures of 500-700°C [33]. Ruthenium films can also be grown from ruthenocene at 595°C but only if hydrogen is present to ensure the removal of carbon [34]. Many of these metallocene precursors have been subsequently reinvestigated [35]. The presence of carbon in the films is often noted; additionally, the metallocenes are very thermally robust precursors and thus the deposition temperatures are usually over 500°C.

Other cyclopentadienyl complexes such as the carbonyls $\text{Cp}_2\text{Ni}_2(\text{CO})_2$, $\text{CpFe}_2(\text{CO})_4$, and $\text{CpMn}(\text{CO})_3$ have been studied [36, 37]. The lack of carbon in the films obtained from $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ was attributed to a disproportionation reaction in which the cyclopentadienyl rings are carried away from the deposition zone as the stable molecule ferrocene [37].

Arene Complexes. Bis(benzene)chromium and its substituted analogues have been studied as sources of chromium metal [36, 38-43]. Depositions conducted at 500°C gave chromium films with carbon levels as low as 0.3%. The arene complex (cycloheptatriene)tricarbonylchromium has also been investigated as a CVD precursor [44].

Allyl and Alkyl Complexes. The metals Pd, Pt, Rh, and Ir form volatile allyl complexes, where the allyl ligand (also known as a propenyl group) has the stoichiometry C_3H_5 . These allyl complexes have been shown to deposit pure metal films at low temperatures [45-48]. The presence of hydrogen during deposition helps to remove excess carbon from the films. Mixed ligand complexes, such as (cyclopentadienyl)(allyl)palladium and (cyclopentadienyl)trimethylplatinum, also serve as CVD sources of Pd and Pt [48-52]. Gold has been successfully deposited from the gold alkyl $\text{AuMe}_2(\text{acac})$ under plasma CVD conditions [53].

Other Precursors for Pure Metals. Alcoxides [54] and acetylacetonates [55-61] of some of the transition metals have been investigated as potential CVD precursors to pure metal films. For example, the complexes $\text{Cu}(\text{acac})_2$ [62-67] and $\text{Ru}(\text{acac})_3$ [30] are reduced by hydrogen under CVD conditions to give metal films, but the ruthenium deposit was shown to contain appreciable amounts of RuO_2 . The rhodium acac complex $\text{Rh}(\text{CO})_2(\text{acac})$ has been shown to give rhodium metal under plasma CVD conditions [68]. Binary complexes containing the trifluorophosphine ligand such as $\text{Pt}(\text{PF}_3)_4$, $\text{Co}_2(\text{PF}_3)_8$, $\text{Rh}_2(\text{PF}_3)_8$, $\text{IrH}(\text{PF}_3)_4$, $\text{Fe}(\text{PF}_3)_5$, $\text{Ru}(\text{PF}_3)_5$, $\text{Cr}(\text{PF}_3)_6$, $\text{Mo}(\text{PF}_3)_6$, and $\text{W}(\text{PF}_3)_6$ have been reported to deposit metal films at temperatures between 200 and 300°C [61, 69-72]. The phosphine complex (cyclopentadienyl) (triethylphosphine) copper deposits copper metal at 200-300°C upon irradiation with a laser [73].

METAL BORIDES

Tetrahydroborates. The tetrahydroborate group, BH_4^- , forms volatile complexes with the group 4 elements titanium, zirconium, and hafnium, and with the lanthanide and actinide elements. Most of the binary tetrahydroborates were prepared in the 1940's and 1950's, and several early patents and articles describe the use of these tetrahydroborate molecules as thin film precursors,

although the deposits were either uncharacterized or only tested for the presence of boron [36, 74-77]. More recently, the identities of the thin films that are obtained upon CVD from $Zr(BH_4)_4$ or $Hf(BH_4)_4$ have been shown to be zirconium or hafnium diboride [78-83]. The films deposited at temperatures between 200 and 400°C are amorphous, although they exhibit electrical conductivities that are close to those of the polycrystalline phase.

For the element titanium, the only known binary tetrahydroborate $Ti(BH_4)_3$ decomposes thermally at -50°C and is unsuited for CVD applications. The stability of this molecule can be increased, however, by the addition of donor molecules. The 1,2-dimethoxyethane adduct $Ti(BH_4)_3(dme)$ is stable at room temperature and sublimes readily. Chemical vapor deposition from this precursor gives thin films of TiB_2 at temperatures as low as 250°C [78].

Other Precursors to Metal Borides. The iron carbonyl cluster $HFe_3(BH_4)(CO)_9$ has been shown to give the spin glass FeSQB20 upon CVD at 175°C [84-85]. The deposition of lanthanide borides has been reported to occur upon passage of the boron hydride $B_{10}H_{14}$ over lanthanide metal powders. In this latter study, it was proposed that decaborane reacts with the lanthanide metals to form a volatile metallaborane intermediate that subsequently acts in situ as a CVD precursor [86].

METAL CARBIDES

Alkyls. The titanium complex tetra(neopentyl)titanium has been shown to serve as a precursor for the deposition of thin films of titanium carbide at temperatures as low as 150°C [87-90]. When the films are grown under a hydrogen pressure of 10^{-2} torr, the Ti:C ratio is 1.00:0.95. The as-deposited films are amorphous, and can be induced to crystallize only at temperatures in excess of 1100°C. The films have been fully characterized by XPS, AES, RBS, SIMS, EXAFS, and electron microscopy. The mechanism of deposition of TiC has also been investigated by kinetic and deuterium labeling studies. The primary step in the CVD pathway involves a-hydrogen elimination to form neopentane and titanium alkylidene intermediates. The chromium alkyl tetra(neopentyl)chromium undergoes CVD to give an amorphous chromium carbide phase [91].

Cyclopentadienyls. Various cyclopentadienyl complexes have been studied as potential CVD precursors to metal carbides. A 1989 patent cited the use of 'titanocene' for the deposition of titanium carbide at temperatures above 500°C, however, the presence of graphite or amorphous carbon in the films was not addressed [33]. Subsequent investigations of the use of cyclopentadienyl complexes of the early transition elements have shown that considerable amounts of graphitic or amorphous carbon are deposited along with the carbide phase [91-98].

METAL SILICIDES

Silyl Complexes. The use of metal silyl ($M-SiH_3$) complexes as CVD precursors to transition metal silicides was pioneered by Aylett in the 1970's [99-105]. The metal silyl complexes

$\text{Co}(\text{SiH}_3)(\text{CO})_4$, $\text{Mn}(\text{SiH}_3)(\text{CO})_5$, $\text{Re}(\text{SiH}_3)(\text{CO})_5$, and $\text{Fe}(\text{SiH}_3)_2(\text{CO})_4$ were shown to deposit films that contained both silicon and the transition metal at temperatures of 200-400°C. The films also contained appreciable amounts of carbon and oxygen, presumably as a result of CO chemisorption.

METAL NITRIDES

Dialkylamides. Many of the precursors that are currently being investigated as potential precursors for the deposition of transition metal nitrides (and oxides, see below) were first prepared by the English chemist D. C. Bradley. Specifically, binary dialkylamides of the transition elements contain direct metal-nitrogen bonds and are often reasonably volatile. The titanium complex $\text{Ti}(\text{NMe}_2)_4$ was claimed in 1975 to serve as a single-source precursor for TiN [106,107], but the deposit obtained was black instead of gold colored, and later studies have shown that the films are heavily contaminated with carbon. More recently, however, the addition of ammonia to the gas streams has been shown to overcome this problem, and good quality films of TiN can be deposited at temperatures above 350°C [108].

Other Precursors to Metal Nitrides. Other compounds that contain direct metal-nitrogen bonds have also been investigated as potential metal nitride precursors. Although the titanium bipyridine complex $\text{Ti}(\text{N}_2\text{C}_{10}\text{H}_{10})_3$ gives deposits that do contain some nitrogen, the films in fact are heavily contaminated with titanium carbide and organic fragments derived from the bipyridine ligands [109-115].

Metal carbonyl clusters that contain nitride groups have recently been studied. The cluster $\text{HFe}_4\text{N}(\text{CO})_{12}$ has been shown to give FeN films at temperatures of 160-180°C [116].

METAL OXIDES

Alcoxide Precursors. Alcoxides of titanium, zirconium, vanadium, tantalum, and copper have been studied as CVD precursors to the metal oxide phases [117-128]. Usually, water or oxygen is added to the CVD gas streams to assist in the removal of the alcoxide ligands and the deposition of carbon-free oxide films. More recently, alcoxide precursors have been used to deposit ferroelectric materials such as PbTiO_3 by co-deposition of a titanium alcoxide with a lead precursor. Other ferroelectric materials have also been grown by this technique [129-131]. A general reference to the use of metal alcoxides as starting materials for solid state oxides has recently appeared [132].

Acetylacetonate Complexes. Perhaps the most generally useful precursors for CVD are the acetylacetonates and complexes of substituted acac ligands such as dipivaloylmethane (dpm), trifluoroacetylacetone (tfacac) and hexafluoroacetylacetone (hfacac). These precursors have been employed to deposit oxide films of elements such as Zr, Hf, Fe, Ni, and Cu at temperatures as low as 450°C [133-139]. The number of published reports that describe the use of acac compounds for the deposition of metal oxides has increased tremendously in the last few years; most of these publications involve the use of acac complexes as sources

for the deposition of high temperature superconductors. Studies directed toward the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [140-151] and the bismuth-containing superconductors [152-154] have recently appeared; plasma-enhanced CVD studies have also been carried out [155, 156]. One advantage of the MOCVD technique is that c-axis oriented films can be laid down that can carry high critical currents. One of the difficulties of the MOCVD approach is that the three or more precursors required for the synthesis of these quaternary and higher phases have different volatilities and decomposition temperatures, but must undergo deposition together. This problem can be overcome by introducing the acac precursors simultaneously into the hot zone through separate feed-ins. Oxygen and water are typically present in the gas stream during deposition. Generally, the deposition temperatures are about 550°C , and the deposits must be post-annealed at 900°C under oxygen to convert them to the superconducting phase. Recently, however, it has been observed that the use of N_2O as an oxygen source during deposition allows the superconducting phase to be grown directly without a post-annealing step.

METAL SULFIDES

Few depositions of transition metal sulfides appear to have been carried out from metal-organic precursors. The tert-butyl thiolate complex of titanium, $\text{Ti}(\text{S-t-Bu})_4$, is reported to decompose under static conditions to TiS [157]. The organic byproducts detected were di(tert-butyl)sulfide and di(tert-butyl)disulfide. In another study, attempts to grow lanthanide sulfides were pursued by passing a mixture of hydrogen sulfide and a β -diketonate complex or a tris(cyclopentadienyl) complex through a hot zone; in both cases, the films contained appreciable amounts of either oxygen or carbon [158].

CONCLUDING REMARKS

To date, the commercial application of transition metal-organic precursors for the deposition of thin films is in its infancy. There are both advantages and disadvantages of using the MOCVD technique for the deposition of thin films that contain transition metals [159]: although the processing temperatures can often be lowered below those typical of methods that involve metal halide precursors, the deposition process may be considerably more difficult to engineer and the resultant film often contains excess carbon or other undesirable heteroatoms. Nevertheless, there is reason to expect that these difficulties will be largely overcome. Metal-organic CVD precursors for main-group elements have largely supplanted halide precursors in the growth of compound semiconductors such as GaAs and InP, and it is possible that the next twenty years will see a similar increase in the use of transition metal-organic compounds as CVD sources.

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