TAILORED ORGANO METALLICS AS LOW-TEMPERATURE CVD PRECURSORS TO THIN FILMS

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ABSTRACT

We have been investigating the use of "tailored" organo-metallc precursors for the chemical vapor deposition (CVD) of thin films in an effort to open up new approaches to the low-temperature synthesis of ceramic, electronic, and optical materials that contain transition metals. Following our approach to the successful deposition of high-quality titanium carbide thin films at 150-250°C from tetraneopentyltitanium, we have extended this technique to the preparation of other carbides, such as ZrC, HfC, TaC, and WC, at temperatures some 100°C lower than previous CVD methods from the metal halides and methane. The details of the thermolysis of the organometallic precursors are most consistent with a mechanism involving homolysis of M-C bonds to give alkyl radicals followed by C-C and C-H bond activation steps. Metal diboride thin films such as TiB$_2$, ZrB$_2$, and HfB$_2$ can be prepared at ca. 250°C by CVD of suitable tetrahydroborate precursors: Ti(BH$_4$)$_3$-(MeOCH$_2$CH$_2$OMe), Zr(BH$_4$)$_4$, and Hf(BH$_4$)$_4$. In these cases, the principal byproducts are hydrogen and diborane. Mirror-bright, adhesive thin films up to 2 µm thick can be grown on a variety of substrates including glass, steel, aluminum, copper, silicon, and graphite. Despite the amorphous nature of the films, their electrical resistivities are essentially identical with those of the bulk polycrystalline material.

INTRODUCTION

The fabrication of electronic devices by chemical vapor deposition is a rapidly expanding area of great current interest. Metal-organic chemical vapor deposition (MOCVD) routes to the preparation of semiconductor thin films are becoming increasingly attractive, as for example in the preparation of GaAs from GaMe$_3$ and AsH$_3$ [1,2]. However, despite the intensive study of the syntheses of main-group materials by MOCVD, relatively few studies of the deposition of thin films that contain transition metals have been reported [3-10]. Herein we describe an overview of our approach to the rational design of organometallic CVD precursors to thin films of metal carbides and borides; this technique allows the deposition of high-quality ceramic films at temperatures some 1000°C lower than those possible by previous methodology.

Titanium carbide, TiC, and titanium boride, TiB$_2$, have found wide use as protective coatings for metal cutting tools and in the aerospace industry, as low-friction coatings for bearings, and in the case of TiB$_2$, as crucibles and electrodes in metal refining equipment such as aluminum reduction cells.
These applications arise from their desirable properties: high hardness, high melting point, moderate strength, resistance to wear and corrosion, and good electrical conductivity. Conventionally, the coatings are deposited in a gas phase CVD process from TiCl$_4$ and methane for TiC, or TiCl$_4$ and BCl$_3$ for TiB$_2$; hydrogen is usually added as a reductant [11]. These processes, which were discovered in the 1920's and 1930's, operate at temperatures in excess of 1000°C due to the relatively high thermal stability of the molecular precursors.

\[
\text{TiCl}_4 + \text{CH}_4 \rightarrow \text{TiC} + 4\text{HCl}
\]
\[
\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2 + 10\text{HCl}
\]

A principal advantage of employing organometallic precursors is that they are far more reactive thermally than metal halides and related species, and therefore may lead to far lower processing temperatures for CVD. This fact provides the motivation for studying organotransition metal species as precursors to ceramic, electronic, and optical materials. (Note: We use the word "organometallic" according to its true meaning to describe molecules possessing direct metal-carbon bonds.)

There are potentially several different processing methods other than CVD by which organometallic precursors could be converted to ceramic materials, and in general, these may be classified into solid state, solution, and gas phase techniques. Among solid state thermolytic methods are the "pre-ceramic" polymer technique, spin-casting, and solution evaporation techniques; in all of these, the immediate precursor to the ceramic final product is a solid inorganic or organometallic species. The solid state methods are attractive due to their technical simplicity, but the ceramic product is often not a single phase material, and usually possesses severe mechanical defects due to the blistering and fracturing that arise upon outgassing of the volatile by-products during thermolysis. In all these solid state methods, a high-temperature firing step is usually required to obtain a useful material. Among solution techniques are solution thermolytic methods, sol-gel processing, molten salt techniques, and electrodeposition methods, and all are the subject of intense investigation, although usually with inorganic rather than organometallic precursors.

In comparison, gas-phase CVD is a very attractive deposition method and has several advantages over the solid and solution phase methods described above, and over other gas-phase techniques, such as physical vapor deposition or sputtering [11]. In particular, the atom-by-atom nature of the deposition process eliminates outgassing problems and often results in high film quality. Furthermore, high growth rates, high purity, and ease of process control are characteristic of the MOCVD method, along with low operating temperatures, given suitable molecular precursors.
DESIGN OF ORGANOMETALLIC AND RELATED CVD PRECURSORS

The choice of a molecular species that is likely to serve as an efficient CVD precursor at low temperatures is dependent on a variety of factors. Not all potential precursors thermolyze cleanly to give spatially uniform, strongly adherent, and chemically homogeneous films. The choice of a molecular precursor must take into account such factors as the physical properties of the precursor, ease of synthesis and handling, and the probable mechanism of thermolysis. Some of the more important considerations are discussed below.

1) Volatility. Relatively few organotransition metal complexes are appreciably volatile, and this fact places a severe restriction on the number of available MOCVD precursors. High molecular weight and ionic complexes are almost without exception ruled out for this reason, and only a small fraction of electrically neutral organometallic species are sufficiently volatile to be potential CVD candidates. For example, the presence of phenyl-substituents in a metal complex usually increases the lattice energy, and renders the compound non-volatile. Additionally, ligands that are very loosely held are also inadvisable, since they tend to dissociate upon heating before volatilization of the precursor can begin. The best candidates for CVD precursors are electrically neutral low molecular weight species that do not have labile ligands or exhibit strong intermolecular interactions in the solid state.

2) Mechanistic Considerations. The conversion of a CVD precursor to a useful thin film involves stripping of most of the coordinated ligands, often with concomitant fragmentation reactions that leave behind interstitial heteroatoms such as C, B, N, O, etc. The details of the thermolytic decomposition mechanism will dictate whether the precursor undergoes desirable chemical reactions that lead to a pure ceramic product, or whether films of undesirable composition, constitution, or properties will result. The efficacy of the CVD process depends critically on the proper choice of coordinated ligands that will allow thermolysis to occur via chemically productive pathways and with low activation barriers.

For example, while it has been known since Mond discovered Ni(CO)₄ in 1890 that nickel films may be prepared readily by thermolysis of the carbonyl, early transition metal films cannot be prepared in this fashion. Instead, attempted deposition of films of early transition metals such as molybdenum from Mo(CO)₆ give molybdenum oxides and graphite. This results from the facile chemisorption of carbon monoxide on metal surfaces to give surface-bound oxide and carbide atoms; subsequent reactions give the observed products. Accordingly, binary metal carbonyls are in general unsuited for CVD except for late transition metals such as Ni, Co, and Fe[10].

Another large class of organometallic complexes are the cyclopentadienyls, and in fact quite pure ruthenium films have been prepared from Cp₂Ru by CVD at 500°C [7]. However, the cyclopentadienyl group is generally very tightly bonded to transition metal centers and loss of the Cp ligand is a high energy process. Furthermore, the condensed π-system can it-
self undergo decomposition under CVD conditions to give films contaminated with graphitic inclusions. Similar carbon inclusions were noted in early attempts to grow chromium films from the arene complex dibenzene chromium [8].

Approaches to the CVD of metal nitrides, oxides, sulfides and related species must take into consideration the source of the heteroatom, and the potential for side reactions. For example, attempts to prepare TiN by CVD from the coordination complex Ti(bipyridine)$_3$ result instead in the deposition of titanium carbide that contains small amounts of TiN and rather larger quantities of aromatic hydrocarbons that result from fragmentation of the bipyridine rings [12]. The predominant formation of TiC rather than TiN is not surprising in view of the thermodynamic stability of the carbide and the lack of thermolytic pathways that would selectively remove nitrogen from the bipyridine ring. Earlier claims [13] of the deposition of TiN from the titanium amide precursor Ti(NMe$_2$)$_4$ are in fact erroneous; in our hands the principal CVD product is TiC. This is fully consistent with the known chemistry of M(NR$_2$)$_x$ complexes; specifically, loss of HNR$_2$ and formation of metal-

\[
\begin{align*}
M & \text{NMe}_2 \\
\rightarrow & \\
M & \text{CH}_2 + \text{NMe}_2
\end{align*}
\]

lacyclic Ti-C bonds is a primary thermolytic process [14]. Indeed, it is in general a non-trivial problem to avoid the formation of early transition metal carbides when using hetero-atom-containing organometallic species as CVD precursors.

There is a third class of organometallic complexes that avoids the use of carbonyl or cyclopentadienyl groups: these are the transition metal alkyls and related hydride species. Whereas main-group alkyls such as GaMe$_3$ and ZnMe$_2$ have long been used in MOCVD depositions, transition metal alkyls are not commercially available and perhaps for this reason had not been studied as thin film precursors before our studies began in 1987 [3,4].

**CARBIDES AND BORIDES OF TITANIUM, ZIRCONIUM, AND HAFNIUM**

Of the potential organometallic precursors for carbides of the group 4 elements, such as Cp$_2$TiMe$_2$, Cp$_2$Ti(CO)$_2$, Ti-(C$_6$H$_6$)$_2$, Ti(CH$_2$SiMe$_3$)$_4$, and Ti(CH$_2$Ph)$_4$ [15], we chose the titanium alkyl tetra(neopentyl) titanium, Ti(CH$_2$CMe$_3$)$_4$, and its zirconium and hafnium analogues (Figure 1) based on the considerations described above [3,4]. Specifically, the neopentyl complexes are appreciably volatile, and contain no carbo-cyclic rings such as Cp, or heteroatoms such as O or Si. Furthermore, neopentyl groups are known [16,17] to undergo C-H and C-C bond cleavage reactions that we felt provided an opportunity for the formation of the metal carbide without graphitic inclusions. Passage of M(CH$_2$CMe$_3$)$_4$ through an externally heated Pyrex high-vacuum apparatus (Figure 2) resulted in the deposition of adhesive thin films of TiC, ZrC,
Figure 1. Molecular structure of Ti(\(\text{CH}_2\text{CMe}_3\))_4.  

Figure 2. Diagram of high-vacuum (10^-7 torr) CVD apparatus.  

Figure 3. Molecular structure of Ti(BH_4)_3(dme).
or HfC on Pyrex glass slides mounted in the hot zone. The optimum deposition temperatures of 250°C for TiC, and ca. 400°C for ZrC and HfC are some 1000°C lower than those characteristic of prior CVD methods from the metal halides. The characterization of these films has been described more fully elsewhere [3,4].

Studies of the gases evolved during the deposition of TiC films by MOCVD show that the major product is neopentane (93-97%). Smaller amounts of other hydrocarbons such as isobutylene (0-3%), propene (0-3%), 2,2,5,5-hexamethylhexane (0-0.5%), and 2,2,5,5-hexamethyl-3-hexene (0-1%) are also formed, although the latter neopentyl coupling products only appear at high pressures. Since the Ti-C bond is substantially weaker [18] than C-C or C-H bonds (ca. 45 kcal mol⁻¹ vs. ca. 100 kcal mol⁻¹), Ti-C bond homolysis is a likely first step in the thermolytic mechanism. The higher deposition temperatures necessary for Zr(CH₂CMe₃)₄ and Hf(CH₂CMe₃)₄ are consistent with this hypothesis since the M-C bond strengths of ca. 55 kcal mol⁻¹ are substantially higher in these molecules. Furthermore, tetra(alkyl)lead species are well-known to decompose by Pb-C bond cleavage to yield alkyl radicals, and the Pb-C bond strength in PbMe₄ of ca. 40 kcal mol⁻¹ is comparable with those in Ti(CH₂CMe₃)₄.

Borides of the group 4 elements of stoichiometry MB₂ should be accessible by CVD of a corresponding metal tetrahydroborate. Tetrahydroborates, although not organometallic species by definition, are the simplest boron-containing molecular derivatives of the transition elements, and compounds such as Zr(BH₄)₄ and Hf(BH₄)₄ have long been known, are quite volatile, and are natural CVD candidates. In fact, there have been a few reports of the use of the zirconium and hafnium compounds as CVD precursors, but until recently, the deposition temperatures employed were well over 5000°C and the ceramic products have not been well characterized [19-26]. For titanium, however, the choice of a precursor is not as straightforward. The tetravalent compound Ti(BH₄)₄ does not exist (TiIV is reduced by BH₄⁻), and trivalent Ti(BH₄)₃ is unstable above -50°C and is only available in milligram quantities [27]. We have investigated thermally more stable phosphine adducts such as Ti(BH₄)₃(Me₂PCH₂CH₂PMe₂)₂ [28] and Ti(BH₄)₃(PMe₃)₂ [29], but find that the phosphine ligands are too labile, and loss of BH₃·PR₃ leads to decomposition of the precursors before volatilization begins. We accordingly turned to ether adducts of Ti(BH₄)₃ since Ti-O bonds are stronger than Ti-P bonds (thus reducing the lability), while the BH₃·OR₂ bond enthalpy of 10 kcal mol⁻¹ is less than the 20 kcal mol⁻¹ typical of BH₃·PR₃ compounds.

The tetrahydrofuran adduct Ti(BH₄)₃(OC₄H₈)₂ is volatile without decomposing at 250°C, and uniform films may be obtained by CVD from this precursor. The TiB₂ films so obtained contain appreciable amounts of carbon and oxygen (> 10%), and this is attributed to a ring-opening reaction of the tetrahydrofuran ligands to give butoxy groups:

\[
\begin{align*}
\text{H} & \quad \text{Ti-O} \\
& \rightarrow \quad \text{Ti-O-} \\
& \rightarrow \quad \text{Ti,O,C + hydrocarbons}
\end{align*}
\]
This problem was overcome by employing an acyclic ether, and we chose 1,2-dimethoxyethane, MeOCH₂CH₂OMe or dme. The adduct Ti(BH₄)₃(dme) (Figure 3) is sublimable at 25°C, and very pure films of TiB₂ may be obtained at temperatures of 200 - 250°C. The dme ligand dissociates intact from the titanium in the hot zone and does not make a BH₃·dme adduct or otherwise participate in the reaction chemistry under the deposition conditions. The generated Ti(BH₄)₃ fragment thermolyzes to give good quality TiB₂ films and B₂H₆ and H₂ as byproducts (detected mass spectrometrically). The levels of oxygen and carbon are at the detection limits for XPS and Auger spectroscopy (<1%). The titanium and boron XPS binding energies match those of bulk TiB₂, while the Auger results confirm the Ti:B ratio of 1:2.0 (Figures 4 and 5). Scanning electron micrographs
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<td>ZrB₂</td>
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Table I  Electrical resistivities of MB₂ films.

reveal an essentially featureless film morphology (Figure 6), and the films are 0.5 - 1.0 μm thick as measured by an alpha-step analyzer. Surprisingly, despite the fact that X-ray diffraction shows the films to be amorphous, electrical measurements give resistivities of 12 μΩ-cm that are essentially identical with the values of 9 - 15 μΩ-cm for polycrystalline TiB₂ (Table I). Therefore, while the lattice must be disordered, enough of the TiB₂ layer structure must be intact to give good electrical conduction over macroscopic distances. Evidently, small (sub-nanometer) domains of the TiB₂ structure must be interconnected so as to preserve the conduction network of the boron layers, but must be misoriented slightly with respect to each other to destroy any longer-range order.

In similar studies, high-quality films of ZrB₂ and HfB₂ may be grown from the M(BH₄)₄ precursors on a variety of substrates including glass, copper, aluminum, steel, graphite, and silicon at 250°C and 10⁻⁴ torr. Auger and XPS spectra of the films obtained are essentially identical with those of analogous films prepared at >1000°C.

We are continuing our efforts to determine the mechanisms of the deposition processes, to measure the physical properties of the films prepared by the "tailored" precursor approach, and to extend the applicability of this technique to the synthesis of other thin film materials.

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REFERENCES


