Titanium carbide, TiC, and titanium diboride, TiB₂, have found wide use as protective coatings for cutting tools, as low-friction coatings for bearings, and in the case of TiB₂, as high emissivity coatings in the aerospace industry and as crucibles and electrodes in metal refining equipment such as aluminum reduction cells [1-3]. These applications arise from their desirable properties: high hardness, high melting point, moderate strength, resistance to wear and corrosion, and good electrical conductivity. These properties are retained even at high temperatures [4-6]. Conventionally, thin films are deposited in a gas phase chemical vapor deposition (CVD) process from TiCl₄ and methane for TiC, or TiCl₄ and BCl₃ for TiB₂; hydrogen is usually added as a reductant [4-7].

\[
\begin{align*}
\text{TiCl}_4 + \text{CH}_4 & \quad 1200^\circ\text{C} \quad \rightarrow \quad \text{TiC} + 4\text{HCl} \\
\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 & \quad 900^\circ\text{C} \quad \rightarrow \quad \text{TiB}_2 + 10\text{HCl}
\end{align*}
\]

The high temperature required to overcome the relatively high thermal stability of the molecular precursors also precludes coating precision machine parts and thermally fragile substrates.

A principle advantage of employing organometallic precursors is that they are far more thermally reactive than metal halides, and therefore may lead to far lower processing temperatures for CVD. For example, the titanium alkyl, tetra-2-propyl titanium, Ti(CH₂CMe₃)₄, when sublimed through an externally heated Pyrex high vacuum apparatus forms a highly reflective metallic film of TiC on substrates at 250°C [8]. This low deposition temperature is nearly 1000°C lower than those characteristic of prior CVD methods from the metal halides. Auger (AES), and X-ray diffraction indicate the films are amorphous with a stoichiometry of TiC₀.₉₃. X-ray photoelectron spectroscopy (XPS) results indicate that the observed Ti 2p₃/₂ peak at 455.1 eV and the C 1s peak at 281.6 eV do correspond to a TiC phase. The gaseous byproducts, as detected by GC/MS, are neopentane (95%), and small amounts of isobutylene and propene. These products are consistent with a radical decomposition mechanism.

Diborides of the Group IV elements have been prepared by using metal tetrahydroborate complexes as precursors. The compounds Zr(BH₄)₄ and Hf(BH₄)₄ have long been known and are quite volatile [9]. Amorphous MB₂ films can be prepared with a substrate temperature of 250°C.

For titanium diboride, the choice of precursor was not so straightforward. The tetravalent compound Ti(BH₄)₄ does not exist (Ti^IV is reduced by BH₄⁻), and trivalent Ti(BH₄)₃ decomposes autocatalytically below room temperature and can only be prepared in milligram quantities [10]. The thermally stabilized phosphine adducts Ti(BH₄)₂(dmpe)₂ [11] and Ti(BH₄)₃(PMe₃)₂ [12] were considered as precursors. However, these precursors readily lose BH₄⁻PR₃ prior to volatilization and intractable residues result. Ether adducts of Ti(BH₄)₃ were also considered since Ti-O bonds are stronger than Ti-P bonds (thus reducing the
lability), while the BH$_3$·OR$_2$ bond enthalpy of 10 kcal mol$^{-1}$ is less than the 20 kcal mol$^{-1}$ typical of BH$_3$·PR$_3$ compounds.

The 1,2-dimethoxyethane adduct Ti(BH$_4$)$_3$(dme) can be prepared by action of NaBH$_4$ on TiCl$_4$ in dme. Infrared and single crystal X-ray diffraction studies indicate the molecule has three bidentate tetrahydroborate groups arranged in a pseudo trigonal bipyramidal geometry.

$$\text{TiCl}_4 + 4 \text{NaBH}_4 \xrightarrow{\text{dme}} \text{Ti(BH}_4)_3(\text{dme}) + 4 \text{NaCl} + 1/2 \text{B}_2\text{H}_6 + 1/2 \text{H}_2$$

$$\text{Ti(BH}_4)_3(\text{dme}) \xrightarrow{200^\circ\text{C}} \text{TiB}_2 + \text{dme} + 1/2 \text{B}_2\text{H}_6 + 9/2 \text{H}_2$$

The complex Ti(BH$_4$)$_3$(dme) sublimes at 25°C, and pure amorphous films of TiB$_2$ may be obtained at 200°C on a variety of substrates including: glass, copper, steel, aluminum, graphite, and silicon [13]. Mass spectrometry indicates the dme ligand dissociates intact from titanium in the hot zone and does not participate in the reaction chemistry. XPS and AES spectra indicate only trace carbon and oxygen impurities; the AES data confirm a Ti:B ratio of 1:2.07. The electrical resistivity of the films has been measured at 12 µΩ·cm. Bulk TiB$_2$ has a resistivity value of 9-15 µΩ·cm.

References


