Organometallic Route to the Chemical Vapor Deposition of Titanium Carbide Films at Exceptionally Low Temperatures

Gregory S. Girolami,* James A. Jensen, and Deborah M. Pollina

School of Chemical Sciences
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

Wendell S. Williams,* Alain E. Kaloyeros, and Clare M. Allocca

Department of Physics, Department of Ceramic Engineering
and Materials Research Laboratory
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

Received September 26, 1986

Titanium carbide, TiC, is one of the hardest materials known[1] (9–10 Mohs), possesses remarkable thermal stability (mp 3067 °C), and is essentially unaffected by acids and aqueous alkali.[2] These properties make TiC a very useful material for such diverse applications as first-wall coatings for fusion reactors, protective coatings for cutting tools,[3] and low-friction coatings for bearings.[4] Unfortunately, crystalline TiC is also brittle, and this limits its structural applications at low temperatures.[5] With present industrial technology, only crystalline TiC coatings can be deposited on complex shapes; the commercial process involves chemical vapor deposition from hydrogen, methane, and titanium tetrachloride at 1000 °C.[6] More recently, plasma-assisted chemical vapor deposition[7] techniques have been applied to the synthesis of TiC coatings, but these methods also require high temperatures, in excess of 1200 °C.

We now report a simple and powerful chemical vapor deposition (CVD) method for preparing thin films of TiC using an organometallic precursor at exceptionally low temperatures ($\sim$150 °C). Tetraneopentyltitanium, $Ti[CH_2C(CH_3)_3]_4$,[8,9] was chosen for metal–organic chemical vapor deposition (MOCVD) studies since it volatilizes easily and has been reported to thermolyze at low temperature.[9,10] We have devised an improved synthesis of $Ti[CH_2C(CH_3)_3]_4$: interaction of $Ti(OCH_2CH_3)_4$ with 4 equiv of $LiCH_2C(CH_3)_3$ in pentane followed by sublimation at 50 °C
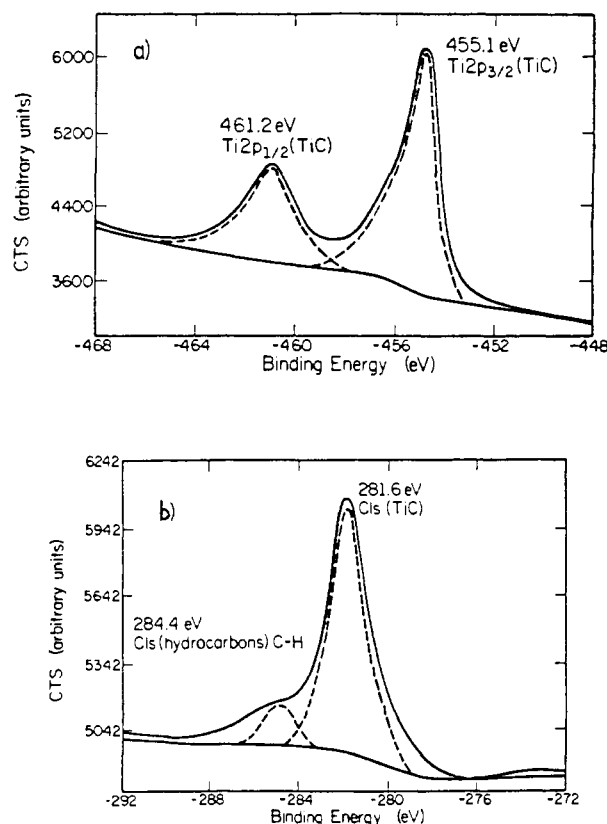

Figure 1. XPS spectra from titanium carbide films prepared by MOCVD from $Ti[CH_2C(CH_3)_3]_4$: (a) Ti 2p spectrum showing that TiC is the only titanium-containing species present; (b) C 1s spectrum showing that TiC and small amounts of hydrocarbons are the only carbon-containing species present.

(10^{-3} torr) gives yellow crystals of the titanium alkyl. The use of titanium tetraethoxide as a starting material prevents reduction of the titanium center that occurs upon alkylation of titanium tetrachloride,[9] thereby doubling the yield from 25% to over 50%.

Low-temperature (150 °C) and low-pressure ($<10^{-5}$ torr) chemical vapor deposition of $Ti[CH_2C(CH_3)_3]_4$ was achieved by using a Pyrex high-vacuum apparatus containing an externally heated reaction zone. Passage of $Ti[CH_2C(CH_3)_3]_4$ through the apparatus resulted in the deposition of adhesive thin films of TiC on Pyrex glass slides mounted in the hot zone. Electron diffraction studies of the silvery metallic films showed only broad diffuse rings characteristic of an amorphous solid, while Auger electron spectroscopy (AES) revealed the presence of titanium and carbon in a Ti/C ratio of ca. 1:0.93. The carbon AES signature from the films was qualitatively different from that characteristic of crystalline titanium carbide, indicating a difference in the local atomic environment. X-ray photoelectron spectroscopy (XPS) results indicated that the Ti $2p_{3/2}$ peak at 455.1 eV and the C 1s peak at 281.6 eV (Figure 1) do in fact correspond to a TiC phase.[11,12] Furthermore, small amounts of organic fragments were detected in the coatings, as shown by the C 1s shoulder at 284.4 eV.[13] No oxygen ($<2\%$) or other elements were present in the interior of the films, but some surface oxidation was apparent that resulted in an oxygen atomic concentration of 10% that fell to $<2\%$ within 0.2 μm of the surface. Below this level, there were no changes in the relative elemental amounts or shapes of the XPS peaks as a function of depth within the films.

The thickness of the films can be quite easily tailored by varying the deposition time and temperature. For example, films of 2 μm

(1) Storms, E. K. *The Refractory Carbides*; Academic: New York, 1967; p 3.

(2) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic: New York, 1971; p 141.

(3) Schwarzkopf, P.; Kieffer, P.; Leszynski, W.; Benesovsky, F. *Refractory Hard Metals*; Macmillan: New York, 1953; p 67.

(4) *Refractory Carbides*; Samsonov, G. V., Ed.; Consultants Bureau: New York, 1974.

(5) Williams, W. S. *Prog. Solid State Chem.* **1971**, *6*, 57–118.

(6) Hintermann, H. E.; Gass, H. *Schweiz. Arch. Angew. Wiss. Tech.* **1967**, *33*, 3–10.

(7) Takahashi, T.; Sugimaya, K.; Itoh, H. *J. Electrochem. Soc.* **1970**, *117*, 541–545.

(8) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120–1124.

(9) Davidson, P. J.; Lappert, M. F.; Pearce, R. *J. Organomet. Chem.* **1973**, *57*, 269–277.

(10) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219–242.

(11) Ramquist, L.; Ekstig, B.; Kallne, E.; Noreland, E.; Manne, R. *J. Phys. Chem. Solids* **1969**, *30*, 1849–1860.

(12) Ramquist, L.; Hamrin, K.; Johannson, G.; Gelius, V.; Nordling, C. *J. Phys. Chem. Solids* **1970**, *31*, 2669–2672.

(13) Johannson, L. I.; Hagstrom, A. L.; Jacobson, B. E.; Hagstrom, S. B. M. *J. Electron. Spectrosc. Relat. Phenom.* **1977**, *10*, 259–271.

in thickness may be grown from less than 1 g of $Ti[CH_2C(CH_3)_3]_4$ over 6 h. Faster deposition rates and thicker films can be achieved by raising the temperature above 150 °C. Remarkably, upon dissolution of the Pyrex substrate in hydrofluoric acid, the films are cohesive and retain their integrity despite their largely amorphous nature.[14] Previous MOCVD investigations of TiC films have required higher temperatures and more complicated deposition techniques.[15,16] Furthermore, these films were not single-phase TiC, contained substantial amounts of impurities and lacked cohesiveness upon dissolution of the substrate. Adhesive TiC coatings from $Ti[CH_2C(CH_3)_3]_4$ can also be formed on substrates other than Pyrex such as copper and KBr.

The amorphous TiC films are expected to be resistant to the intergranular decohesion and intragranular cleavage characteristic of polycrystalline samples.[17] However, while the hydrocarbon inclusions and defect sites may make the amorphous films less brittle and more suited for certain applications, they also are expected to significantly decrease the hardness of the TiC coatings. Given this trade off between mechanical strength and hardness, it would be of interest to tailor the properties of the TiC films to suit the application at hand while still retaining the advantage of operating at low temperature. We have found that increasing the pressure above 10^{-4} torr without changing the temperature results in the deposition of *crystalline* TiC coatings as revealed by the carbon AES signature and the presence in the electron diffraction micrographs of sharp, well-defined rings located at the proper TiC d spacing. The physical properties of these crystalline deposits appear similar to the hard but brittle TiC films prepared at conventional, high (1100–1350 °C) temperatures.[7] The absence of hydrocarbon inclusions and associated defect sites in the crystalline films may result from collision-induced stripping of the tetraneopentyltitanium molecules of most of their hydrocarbon ligands in the gas phase before reaching the surface.

One possible mechanism for the deposition of the TiC films produced in the present study involves three principal steps: γ-abstraction in $Ti[CH_2C(CH_3)_3]_4$ with loss of neopentane to give titanacyclobutanes, II, loss of isobutylene from the metallacycle to generate titanium methylene species, III, and hydrogen transfer between methylene groups to give methane and titanium carbide, IV. Most of these steps have precedents in the organometallic
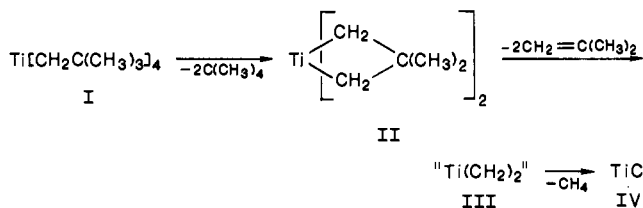
chemistry of early transition metals,[18–21] and neopentane is in fact a product of the thermolysis of $Ti[CH_2C(CH_3)_3]_4$.[9,10] Other mechanisms are, of course, possible and we are currently carrying out labeling studies and complete analyses of the volatile products to determine more precisely the course of the deposition process. One interesting unanswered question is what reactions occur in the gas phase at varying temperatures and pressures before deposition of titanium species on the substrate begins?

(14) Kaloyeros, A. E.; Girolami, G. S.; Allocca, C. M.; Pollina, D. M.; Williams, W. S. submitted for publication in *J. Am. Ceramic Soc.*
(15) Kaloyeros, A. E.; Hoffman, M. P.; Williams, W. S. *Thin Solid Films* **1986**, *141*, 237–250.
(16) Morancho, R.; Constant, G.; Ehrhardt, J. J. *Thin Solid Films* **1981**, *77*, 155–164.
(17) *Glassy Metals*; Güntherodt, H.-J.; Beck, H., Eds.; Springer-Verlag: Berlin, 1981.
(18) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56.
(19) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496.
(20) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204–1211.
(21) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809–810.

These results have shown that TiC films can be obtained by using chemical vapor deposition techniques under very mild conditions. The low temperatures (ca. 150 °C) characteristic of this organometallic route make possible the deposition of TiC films on substrates such as polymers and low-melting metals that are too thermally fragile for other techniques. Extensions of this organometallic route to the synthesis of other early-transition-metal carbides are obvious. Further investigations of refractory coatings are under way; we are particularly interested in the mechanism of the chemical deposition process, the temperature stability and corrosion resistance, and the structure and physics of ordered vs. disordered solids.

The Antiperiplanar Effect in 1,2-Asymmetric Induction

Robert R. Fraser* and Maria Stanciulescu

Ottawa–Carleton Chemistry Institute
University of Ottawa, Ottawa, Canada K1N 9B4
Received May 7, 1986

More than 30 years ago Cram and co-workers formulated a rule for predicting the preferred face of attack by a nucleophile at a carbonyl group adjacent to an asymmetric center.[1] Subsequently, a number of alternate models were put forward by Cornforth,[2] Karabatsos,[3] and Felkin.[4] The four models which represent different rotameric transition states are shown in Figure 1. Later, theoretical calculations by Anh and Eisenstein[5] supported the Felkin model, suitably modified to allow nonperpendicular attack by hydride ion.[6] In arriving at this conclusion, they attributed a key role to the strong energetic preference for an antiperiplanar (app) approach to permit an n–σ* interaction between the pair of electrons of the nucleophile and the σ* antibonding orbital of the antiperiplanar C–L bond.[7] They also compared the relative stabilization energies due to an app C–H, C–C, and C–Cl bond in the transition state for hydride addition. The energies were calculated to be 35.5, 37.4, and 59.0 kcal/mol, respectively (relative to unreacted starting materials). The greater stability of C–C over C–H was attributed to a more favorable n → σ* interaction with the weaker C–C bond (lower energy σ* orbital) and the stabilization by C–Cl to the electronegativity of chlorine. In spite of the fundamental importance of this proposed n–σ* interaction, little theoretical[8] or experimental[9] work has

(1) Cram, D.J.; Elhafez, F. A. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–5835.
(2) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112–127.
(3) Karabatsos, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 1367–1371.
(4) Chêrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2201–2204.
(5) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61–70. See also: Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145–162.
(6) (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067. (b) Bürgi, H. B.; Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1974**, *96*, 1956–1957. Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y. D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science (Washington, D.C.)* **1986**, *231*, 1108–1117.
(7) Anh and Eisenstein described the effect as a π*–σ* interaction that stabilizes the LUMO of the carbonyl group. An alternative interpretation has also appeared. Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552.
(8) Houk, and co-workers accounted for the antiperiplanarity in the addition of hydride ion to propene solely by conformational effects. Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162–7166.
(9) Cheung, C. K.; Tseng, L. T.; Liu, M.-H.; Srivastava, S.; LeNoble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598–1605. Kozikowski, A. P.; Ghosh, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5788–5789. Baldwin, J. E.; Norris, R. K. *J. Org. Chem.* **1981**, *46*, 697–703. Roush, W. R.; Lesur, B.M. *Tetrahedron Lett.* **1983**, 2231–2234.