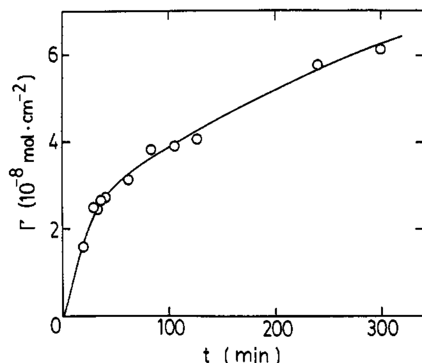

Figure 3. Plot of surface coverage (Γ) vs deposition time (t) for the films of CuPc. Deposition temperature: 90 °C.

the same as those of their powdered sources. Figure 3 shows a plot of Γ vs deposition time (t) for the CuPc film. One of the main features in this plot is that it shows a break at about 40 min, which separates higher and lower growth rate regions.

The investigation of high-temperature aqueous corrosion of Al has been reported by Draley et al.[12-14] They proposed that the corrosion proceeds at the most active cathode spots between Al metal and the air-formed oxide layer: Hydrogen ions in the bulk solution diffuse into the oxide and are reduced to gaseous hydrogen when the ions react at the metal-oxide interface; then the hydrogen gas generates enough pressure to rupture the oxide layer, leading to the breakup of the oxide and the formation of a new oxide layer. In the present research, the liberation of hydrogen gases was also observed in the film-forming experiments. This observation suggests the occurrence of the above-mentioned corrosion reaction at the local cathode of the Al substrate. In our systems, the corrosion of the oxide may be accelerated by the presence of aggressive anions (Br^-) in the dispersion.[15] On the basis of these considerations, the corrosion reaction may cause physical and chemical changes in the aluminum oxide layer, which induces the adsorption of the phthalocyanine particles in the bulk dispersion. At the present stage, adsorption sites on the new oxide layer have not yet been identified; however, the finding that no deposition took place using the dispersion devoid of LiBr suggests that the adsorption site may be a Br^--incorporated spot.

An important and attractive feature of the film-formation processes by the TID method is the fact that phthalocyanine films continue to grow even after the adsorption sites on the Al oxide are covered with a CuPc monolayer, $\Gamma = 2.9 \times 10^{-10}$ mol/cm^2 (Figure 3). One possible explanation for this is that phthalocyanine-Brij 35 aggregates forming an as-grown film may also act as adsorption sites for the next deposition. The elucidation of this film-formation mechanism is now under investigation by varying deposition conditions.

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Registry No. CuPc, 147-14-8; H_2Pc, 574-93-6; Brij 35, 9002-92-0; Al, 7429-90-5.

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Low-Pressure Chemical Vapor Deposition of Tungsten Carbide Thin Films

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Tungsten carbide (WC) is one of the most important constituents of modern cemented materials mostly due to its very high hardness and its exceptional inertness to chemical attack.[1] Previous reports of chemical vapor depositions of WC involved high temperatures (usually 700-1100 °C) and employed precursors ($W(CO)_6$ or WF_6) containing heteroatoms such as oxygen or halogens.[2] Chemical vapor deposition (CVD) from metastable volatile transition-metal compounds might be expected to provide low-temperature routes to thin films. Recently, Girolami et al. reported the CVD production of TiC thin films from the polyalkyl compound $Ti(CH_2CMe_3)_4$.[3] An all-hydrocarbon tungsten complex, e.g., $(Me_3CCH_2)_3W{\equiv}CCMe_3$, **1**, should reduce the heteroatom contamination during CVD production of WC thin films. Moreover, the carbyne carbon in **1** might be expected to be retained in the WC thin films due to the strong W≡C bond in **1**, thereby providing a *single* facile pathway to tungsten carbide. Here we report CVD production of WC thin films from the volatile complex $(Me_3CCH_2)_3W{\equiv}CCMe_3$, **1** (mp 47-48 °C).[4]

Complex **1** was synthesized from $(Me_3CO)_3W{\equiv}CCMe_3$[5] and excess Me_3CCH_2MgCl in ethyl ether and then purified by sublimation at 50 °C and 3×10^{-2} Torr. CVD was performed under vacuum in a quartz hot-wall apparatus (base pressure 4×10^{-3} Torr and 360 °C). The substrates chosen for this study are p-type Si(100) wafers, Pyrex or quartz slides. They were washed with isopropyl alcohol and acetone and then rinsed with distilled water (in the case of the Si wafers, deionized water was used). The substrates were then placed at the center of the hot zone. The precursor was transported at 60-80 °C under vacuum to the deposition chamber. Highly reflective and smooth WC films formed on the substrates and on the wall of the hot chamber at the rate of about 3 μm/h. Gaseous components were collected in a liquid N_2 trap placed before the vacuum pump.[6] They were then vacuum transferred to an NMR tube (C_6D_6 solvent) and analyzed on a Bruker AM500 NMR instrument.

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(6) In the CVD with **2** as precursor, the volatiles condensed in the liquid N_2 trap account for up to 84% of materials based on mass balance. If the deposition chamber is further from the trap, lower mass balances (about 60%) are measured. In all cases, acetone-soluble brown materials are observed. We believe these to be silicon-containing products of transient volatile silicon-containing thermolysis products. See: Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2.

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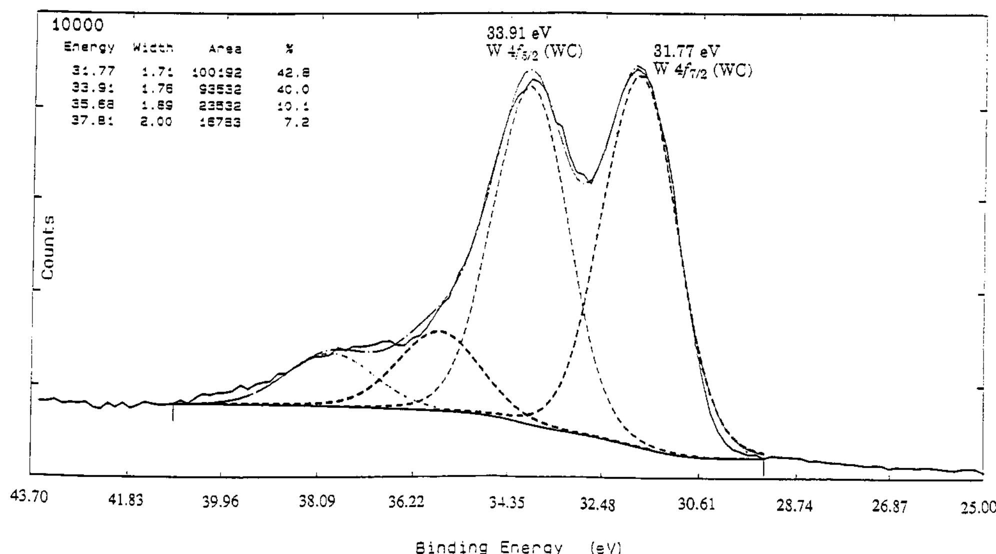
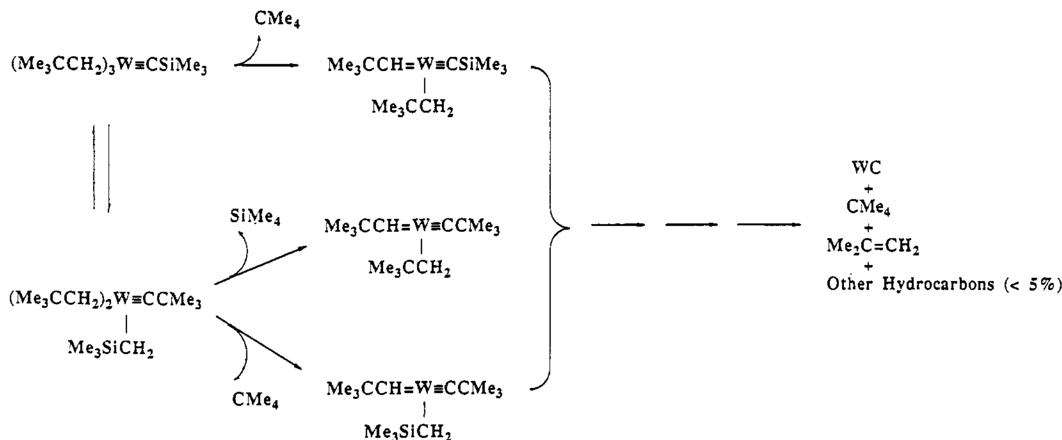


Figure 1. $W(4f_{7/2})$ region of XPS spectrum for a WC thin film on a quartz substrate.

Scheme I. Proposed Mechanism of CVD of Tungsten Carbide from $(Me_3CCH_2)_3W{\equiv}CSiMe_3$, 2a, through α-H Elimination



Powder X-ray diffraction indicates that the films are all amorphous. The thin films on quartz slides remain amorphous after heating under He to 800 °C for 2 h. The thin films on Pyrex strongly adhere to the substrates and are chemically inert. They remain intact after being immersed for 2 weeks in either aqua regia or saturated KOH in isopropyl alcohol. Early studies showed that WC is resistant to acids.[1a,7]

The composition and depth profile analyses of a thin film on quartz were performed by X-ray photoelectron spectroscopy (XPS) on a Surface Science Lab SSX-100 system equipped with a 3-keV Ar^+ sputter gun. The $4f_{7/2}$ line of gold at 84 eV was used for the calibration of the electron-energy analyzer. The XPS data were collected by the monochromatized Al $K\alpha$ excitation with a spot size 600 μm. The film was Ar^+-sputtered to study the bulk composition. Tungsten $4f_{5/2}$ and $4f_{7/2}$ regions are shown in Figure 1. Electron binding energies of 31.77 and 33.91 eV are observed. These correspond to the reported values of 31.7 (W $4f_{7/2}$) and 33.9 eV (W $4f_{5/2}$) for W attached to C in a sputtered WC phase.[8]

Depth profile analysis by XPS and Rutherford backscattering (RBS) indicates that the bulk composition of the film is uniform with a carbon-to-tungsten atomic ratio of 1.1:1. The C_{1s} region of the XPS spectrum shows a broad peak at binding energy of 283.7 eV (half-width 2.1 eV). Reported binding energies for C_{1s} are 282.7 eV for WC and 284.6 eV for graphite.[9] Graphitic carbon could account for the higher carbon content in the WC film from carbon-rich precursor 1. Variable amounts of graphitic carbon have been observed in CVD of TiC from $Ti(CH_2CMe_3)_4$ under vacuum,[3] AlN from $[R_2AlN_3]_3$ (R = Me, Et) or $[Et_2AlNH_2]_3$ under vacuum[10] and TiN from $Ti(NR_2)_4$ (R = Me, Et) at ambient pressure.[11,12] A scanning electron micrograph of the WC thin film on a Si(100) wafer shows a smooth film with particle sizes ranging from 300 to 1000 Å.

NMR analyses of the gaseous components indicate CMe_4 and $Me_2C{=}CH_2$ as the major products in the CVD of $(Me_3CCH_2)_3W{\equiv}CCMe_3$, 1 (supplementary material; see the paragraph at the end of the paper). When CVD of WC thin film was performed with precursor $(Me_3CCH_2)_3W{\equiv}CSiMe_3$, 2,[14] $SiMe_4$ was detected in addition to CMe_4 and

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(12) About 10% oxygen is detected in our WC film by XPS and Rutherford backscattering analysis. Oxygen incorporation from trace amount of O_2 or H_2O has been observed in other CVD systems when base pressure is higher than 10^{-6} Torr.[10,13] We speculate similar incorporation of oxygen by oxophilic tungsten in the WC film, and deposition with a high-vacuum system ($>10^{-6}$ Torr) could eliminate oxygen contamination.
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$Me_2C{=}CH_2$. Similarly, CMe_4 was observed in addition to $SiMe_4$ and $Me_2C{=}CH_2$ in the CVD of WC thin film from $(Me_3SiCH_2)_3W{\equiv}CCMe_3$, **3**. The unexpected presence of $SiMe_4$ and CMe_4 in the CVD from **2** and **3**, respectively, suggests the previously unobserved interconversion of alkyl and alkylidyne groups in $R_3W{\equiv}CR'$. A kinetic/mechanistic study in solution at 100 °C has demonstrated such an exchange and further that the hydrogen atom transfer occurs via an intramolecular mechanism.[15]

A crossover CVD experiment was performed with **1** and $(Me_3CCD_2)_3W{\equiv}CSiMe_3$, **2**-$d_6$. The precursors (1:1 ratio) were placed in two separate sample holders and vacuum transferred simultaneously to the deposition chamber. Mass spectral analysis of gaseous components collected during CVD showed a molecular ion peak of $Me_3SiCD_3^+$ (m/e = 91). No detection of ion peak corresponding to $Me_3SiCD_2H^+$ (m/e = 90) was observed above the isotopic purity of **2**-d_6 (>98% D). Lack of Me_3SiCD_2H in the gas phase is significant in two aspects. First, it shows that $SiMe_4$ production does not proceed significantly through γ-hydrogen elimination. Second, it indicates that unimolecular decomposition is the principal mechanism of tetramethylsilane production in the CVD process.

α-Elimination has been observed in the CVD of TiC thin film from $Ti(CH_2CMe_3)_4$.[16] Our results here are consistent with intramolecular α-elimination as the primary route of decomposition. Considering the alkyl/alkylidyne exchange, we propose the early steps in the CVD production of WC from precursor **2** shown in Scheme I.

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Registry No. $(Me_3CCH_2)_3W{\equiv}CCMe_3$, 68490-69-7; $(Me_3CCH_2)_3W{\equiv}SiMe_3$, 129960-83-4; WC, 12070-12-1.

Supplementary Material Available: Yields of hydrocarbon produced on thermal conversion to WC (1 page). Ordering information is given on any current masthead page.

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Thermal and Oxidative Analyses of Buckminsterfullerene, C_{60}

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Recent developments in the preparation of the fullerene C_{60}[1,2] and discussions of its stability relative to other polycarbon molecules[3] have prompted us to examine its thermal and oxidative behavior. Haufler et al.[3] have proposed that the stability of the fullerene spheroid, relative to a graphitic structure, is due to the absence of dangling bonds typical of those formed along the edges of graphitic layers. This suggestion is consistent with semiempirical[4] and ab initio[5] calculations that conclude that the icosahedral C_{60} molecule is more thermodynamically stable than a graphitic structure. In addition, numerous studies of the kinetics and oxidation mechanism of synthetic graphite have shown that reaction occurs at the edges of layer nets where the atoms are least strongly bonded into the lattice.[6,7] We reasoned, therefore, that the absence of edges and dangling bonds in C_{60} would be expected to impart greater thermal and oxidative stability than is characteristic of graphite. Preliminary reports by Haufler et al.[2] indicate that C_{60} does burn in oxygen; however, to the best of our knowledge, a controlled combustion or oxidation study has not been done.

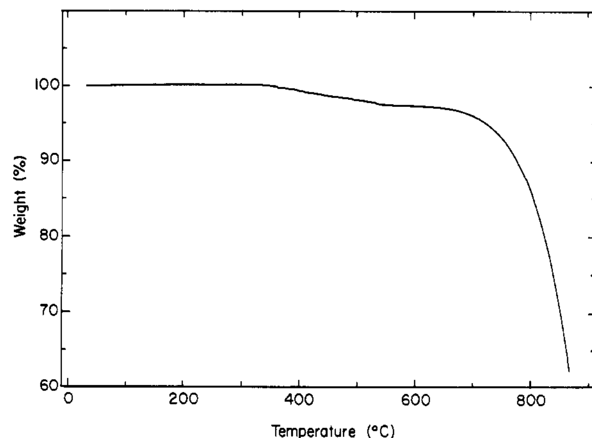

Figure 1. TGA of C_{60} heated at 10 °C/min to 860 °C under N_2 at a flow rate of 50 cm^3/min. Sample had been predried by heating at 300 °C for 0.5 h.

C_{60} was prepared and isolated following the procedures described by Haufler et al.[3] and Aije et al.[8] The C_{60}:C_{70} ratio was greater than 99:1 as determined by negative-ion chemical ionization mass spectrometry. Fisher Scientific G-67 Grade 38 graphite powder was used for comparative studies.

Thermal analyses were performed with a Du Pont Model 2100 thermal analysis system equipped with a thermogravimetric analyzer (TGA). We studied powdered samples (10–12 mg) in air and nitrogen atmospheres at a flow rate of 50 cm^3/min. Initially, samples were dried by heating under nitrogen to 300 °C at a rate of 20 °C/min and holding for 30 min. Subsequent treatment of C_{60} to 860 °C under nitrogen at a heating rate of 10 °C/min demonstrates loss of a volatile component between 300 and 600 °C corresponding to 3–5 wt % (Figure 1). In an effort to identify the volatile component, a sample of C_{60} heated

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