Precursors for Organometallic Chemical Vapor Deposition of Tungsten Carbide Films

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Thin tungsten carbide films were deposited from [HWCp(CO)$_3$], [HWCp*(CO)$_3$], [(*c*yclo*h*epta*t*riene)W(CO)$_3$], [(cycloocta*d*iene)W(CO)$_4$], and [(toluene)W(CO)$_3$] in an ultrahigh vacuum-compatible, cold-wall, low-pressure chemical vapor deposition (LPCVD) reactor. The resultant films were characterized by in situ off-line Auger electron spectroscopy (AES), X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrical resistivity measurements. Films deposited from [HWCp(CO)$_3$], [HWCp*(CO)$_3$], and [(cht)W(CO)$_3$] at 540 °C are amorphous WC incorporating residual graphitic carbon and less than 1 at. % oxygen. WC films can also be deposited from [(cht)W(CO)$_3$] at 350 °C. Films deposited from [(cod)W(CO)$_4$] and [(toluene)W(CO)$_3$] at 540 °C have WC$_{1-x}$ and α-W$_2$C crystalline textures, respectively, and very low oxygen contents.

Introduction

There has been considerable recent interest in organometallic chemical vapor deposition (OMCVD) of refractory films and coatings for microelectronic and tribological applications.[1] Although transition-metal carbide, boride, and nitride films can be deposited by reduction of a volatile metal halide (e.g., WF$_6$ or TiCl$_4$) in the presence of a suitable heteroatom source, such as methane, boron trichloride, or ammonia, the hydrogen halide byproducts are detrimental to process equipment; high deposition temperatures (≥800 °C) are often required; and control of film stoichiometry requires careful adjustments of reactant partial pressures and substrate temperature.[1,2] In contrast, low-temperature OMCVD of transition-metal carbide films can be achieved using single-source molecular precursors. For example, titanium carbide and chromium carbide films have been deposited from the respective tetraneopentyl compounds.[3,4]

Tungsten carbide coatings are used to protect surfaces from erosion and tribological wear, owing to superior hardness, good adhesion, and low friction coefficients; moreover, tungsten monocarbide has excellent chemical and thermal stability.[5] Chemical and thermal stability coupled with low electrical resistivity make tungsten carbides attractive as thin-film diffusion barriers in microelectronic devices.[6,7] As catalysts, tungsten carbides exhibit some of the properties of Pt in hydrocarbon conversion reactions[8] and show electrocatalytic activity for hydrogen oxidation and oxygen reduction.[9]

OMCVD of high-quality tungsten carbide films requires the avoidance of (1) oxygen contamination and (2) co-deposition of amorphous or graphitic carbon. These requirements govern source compound selection and dictate the use of deposition equipment and gases with the lowest possible background contamination levels. The first requirement suggests the selection of organotungsten precursors containing only hydrocarbon ligands; however, cyclopentadienyl (Cp) compounds in particular are apt to result in co-deposition of amorphous or graphitic carbon.[1] Several investigations of organotungsten precursors for tungsten and tungsten carbide CVD have been reported. Unfortunately, low-pressure chemical vapor deposition (LPCVD) reactors with high base pressures (10^{-3} Torr) were employed, and thin-film analysis was performed only after air exposure.

A report of WC deposition from an all-hydrocarbon W complex, [(Me$_3$CCH$_2$)$_3$W≡CCMe$_3$], has appeared.[10] Amorphous films were deposited on Si, glass, and quartz substrates in a hot-wall LPCVD reactor at 360 °C. XPS depth profiling and Rutherford backscattering (RBS) evidenced that the film composition was uniform with a W/C ratio of 0.9. The C$_{1s}$ binding energy (283.7 eV) is intermediate between that of WC (282.7 eV) and graphite (284.6 eV). The primary W 4f peaks are consistent with WC, but peaks at higher binding energy were observed, consistent with the presence of about

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Table 1. Typical OMCVD Conditions

compound	source temp, °C	deposition time, min	deposition temp, °C (range)[a]	reactor pressure mTorr
$HWCp(CO)_3$	90	1−60	540 (480−700)	7.0
$HWCp^*(CO)_3$	105	60	540 (500−700)	1.5
$(cht)W(CO)_3$	115	30−60	540 (350−700)	1.3
$(cod)W(CO)_4$	115	30−60	540 (350−700)	3.0
$(toluene)W(CO)_3$	90	30−60	540 (400−600)	7.5
$W(CO)_6$	65	0.5−20	540 (350−600)	15.0

[a] Indicates range of substrate temperatures which was investigated.

10 at. % oxygen in the films. The principal volatile products were neopentane and 2-methylpropene. Mechanistic studies were consistent with α-hydride elimination as the primary thermolysis pathway.

Kirss et al.[11] used tetraallyltungsten [$W(\eta^3\text{-}C_3H_5)_4$] to deposit amorphous tungsten carbide films on glass and silicon substrates at 300−400 °C and 10−20 mTorr in a hot-wall short-path reactor. The films contained 40 at. % W, 44 at. % C, 10 at. % O, and 6 at. % Si, as revealed by AES depth profiling. The resistivities of the as-deposited films were high ($>1\ \Omega$ cm). Analysis of volatile byproducts revealed that 95% was propane and propene. Thermolysis pathways involving α-hydride elimination or vinylic C−H activation were proposed to explain the results.

[$CpW(CO)_3(CH_3)$] and [Cp_2H_2W] were investigated as precursors for W OMCVD in a cold-wall reactor at 1.5 Torr.[12] The precursors were sublimed into an equimolar H_2/N_2 carrier stream; the partial pressure was typically 20−30 mTorr. Films were deposited from [Cp_2H_2W] and [$CpW(CO)_3(CH_3)$] at 540 and 450 °C, respectively. The resultant films contained 5−15 at. % carbon and 5−10 at. % oxygen and had closely similar morphologies, irrespective of the precursor. XRD measurements revealed that the films typically comprised β-W, a low-temperature metastable phase associated with oxygen impurities. The XPS binding energy indicated that the presence of only carbidic carbon within the films.

In contrast to the above results, we found that films containing >95 at. % W, about 4 at. % carbon, and only 1 at. % oxygen can be deposited from [$W(CO)_6$] at 540 °C by employing a UHV-compatible LPCVD reactor.[13] The low oxygen content of these films motivated us to investigate organotungsten derivatives of [$W(CO)_6$] as single-source precursors for tungsten carbide OMCVD. The compounds [(cycloheptatriene)$W(CO)_3$], [(cyclooctadiene)$W(CO)_4$], and [(toluene)$W(CO)_3$] are synthesized in high yields from [$W(CO)_6$] by replacing two or three of the carbonyl ligands with a single olefinic or aromatic ligand. [$HWCp(CO)_3$] and [$HWCp^*(CO)_3$] also were investigated, and the results are compared to those reported previously for [$(CH_3)WCp(CO)_3$].[12]

Experimental Methods

General Procedures. The organotungsten compounds were synthesized according to procedures described in the literature. All manipulations were effected using standard Schlenk and drybox techniques under an N_2 atmosphere. Briefly, [$HWCp(CO)_3$] was synthesized by treatment of [$W(CO)_6$] with [NaCp] in tetrahydrofuran (THF), followed by acidification of the resultant solid with acetic acid.[14−16] [$W(CH_3CN)_3(CO)_3$] and [$W(C_2H_5CN)_3(CO)_3$],[17−20] which were synthesized from [$W(CO)_6$], were used as intermediates in the syntheses of [$HWCp^*(CO)_3$],[14,21] [(cht)$W(CO)_3$],[14] [(cod)$W(CO)_4$],[14] and [(toluene)$W(CO)_3$][14] by reacting either [$W(CH_3CN)_3(CO)_3$] or [$W(C_2H_5CN)_3(CO)_3$] with the corresponding ligand. The crude reaction products were purified by sublimation, and the purity was checked by infrared spectroscopy.[13] [$HWCp(CO)_3$] sublimes readily at 60 °C and 0.1 Torr, and the remaining compounds sublime at 80−90 °C and 0.1 Torr. The precursors were stored in N_2-filled MBraun drybox prior to use.

The 25-mm Si(100) substrates were cleaned using the following procedure: a 10-min UV/air treatment to remove hydrocarbons and grow a thin photochemical oxide layer,[22] a 60-s dip in 1% HF solution to remove the oxide, and a final 5-min DI water rinse. After two cleaning cycles, the substrate was mounted on a stainless steel sample holder and transferred into the reaction chamber via a load lock. Substrates covered by a thin photochemical SiO_2 layer were prepared by a final 10-min UV/air treatment after one cleaning cycle.

Film Deposition and Characterization. The low-pressure chemical vapor deposition (LPCVD) reactor (10^{-7} Torr base pressure) is fully described elsewhere.[13] The reactor was constructed from a 6-way, 2.5-in. i.d. tubing cross and evacuated by an 310-L/s Edwards turbomolecular pump. The reactor pressure was controlled by a manual butterfly valve and measured by an MKS capacitance manometer.

Films were deposited on Si substrates under the conditions listed in Table 1. The precursor (0.5−1.0 g) was loaded into a Pyrex tube in the drybox, the tube was attached to a Conflat miniflange, and the contents were isolated from the air by two stainless steel bellows valves. The source tube assembly was removed from the drybox and connected to the LPCVD reactor via VCR fittings. The tube was evacuated several times at ambient temperature until a base pressure of 10^{-5}−10^{-7} Torr was achieved, depending on the volatility of the precursor. The source compound was sublimed directly into the reactor under dynamic vacuum. No carrier gas or buffer gas was used, thus avoiding a potential source of oxygen contamination. As [$HWCp(CO)_3$] melts at approximately 68 °C,[14] it was present as a liquid in the source tube during LPCVD.

After deposition, each sample was transferred via the load lock to an ultrahigh vacuum chamber (10^{-10} Torr base pressure) for surface analysis and annealing (if desired). Auger electron spectroscopy (AES) measurements were made using a Physical Electronics (PHI) 3017 PC AES subsystem comprising a 10−155 single-pass cylindrical mirror analyzer with coaxial electron gun and associated electronics. The primary electron beam energy was 3 keV. To study the bulk composition, AES depth profiling was performed using a PHI 04-303

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Table 2. Compositions of the Films Deposited from Organotungsten Compounds

source compound	deposition temp (°C)	(S)urface (B)ulk	Si (at. %)	W (at. %)	C (at. %)	O (at. %)	ref
$HWCp(CO)_3$	540	S	0	30	69	1	this work
		B	0	46	53	<1	
$(CH_3)WCp(CO)_3$	320−620	B	0	>75	5−15	5−10	12
$HWCp^*(CO)_3$	540	S	0	23	75	1	this work
		B	0	42	57	1	
$(cht)W(CO)_3$	540	S	0	37	61	1	this work
		B[a]	0	40−45	55	<5	
	350	S	0	42	55	3	
		B[a]	4	44	43	9	
$(cod)W(CO)_4$	540	S	0	56	39	5	this work
		B[a]	0	65	35	<1	
$(toluene)W(CO)_3$	540	S	0	64	24	12	this work
		B	0	70−75	20−25	5	
$W(C_3H_5)_4$	300−400	B[a]	6	40	44	10	11
$(Me_3CCH_2)_3W{\equiv}CCMe_3$	360	B[a]	0	43	47	10	10
$W(CO)_6$	375	S	0	52	31	17	13
		B	0	76	17	8	
	540	S	0	70	2	10	
		B	0	>95	<4	1	

[a] Film exposed to air prior to depth profiling.

5-kV differential ion gun and 11-065 controller; a 5-keV Ar ion beam was generated at 1×10^{-6} Torr using a 2.5 mA emission current. Atomic concentrations were evaluated from the peak-to-peak intensities of the O(KLL, 503 eV), Si(LMM, 92 eV), C(KLL, 272 eV), and W(NNN, 179 eV) AES transitions in the derivative spectra. Handbook AES sensitivity factors were used.[23] The carbon(KLL) AES line shape was used to evaluate the relative concentrations of carbidic and graphitic carbon in the films. In addition to the principal carbon-($KL_{23}L_{23}$) AES transition at 271 eV, peaks at 254 eV (KL_1L_1) and 261 eV (KL_1L_{23}) are indicative of carbidic carbon. A local minimum at 240 eV due to a $\sigma + \pi$-plasmon loss is associated with graphitic carbon.[24,25]

The morphology and thickness of the films were determined by using a JEOL 6400 field-emission scanning electron microscope (FESEM) in a nearby lab. A Rigaku X-ray diffractometer (XRD) was used for thin-film diffraction measurements. The sheet resistances of the films were measured using a Magne-Tron M-700 four-point probe.

Results

Cyclopentadienyl(tricarbonyl)tungsten Hydride. Carbon-rich tungsten carbide films are deposited on Si from [$HWCp(CO)_3$] at 540 °C and 7 mTorr. A minimum substrate temperature of 500 °C is required for the deposition of continuous films, as evidenced by AES. We infer from the C(KLL) Auger line shape that the surface carbon is predominantly graphitic at temperatures ≥500 °C. The surface oxygen concentration decreased with increasing substrate temperature, falling below the AES detection limit at 700 °C. For films deposited at 540 °C, the surface W/C ratio is approximately 0.45 with only 1 at. % oxygen (Table 2).

For films deposited from [$HWCp(CO)_3$] at 540 °C, two compositionally distinct layers are observed: a carbon-rich surface layer and an underlying tungsten carbide layer of relatively uniform composition. Figure 1 shows AE spectra which were recorded after the indicated Ar^+ sputtering times; the concentration−depth profile is shown in Figure 2a. As evidenced by the C(KLL) line shape, the bulk region contains predominantly carbidic carbon. The bulk W/C ratio is approximately 0.9, and the oxygen concentration is less than 1 at. %. The Si−WC interface is relatively sharp, but the as-deposited film is not an effective diffusion barrier. Annealing in vacuo at 900 °C results in out-diffusion of Si and in-diffusion of W and C as evidenced by the depth profile (Figure 2b); consequently, the bulk W/C ratio is reduced to about 0.7.

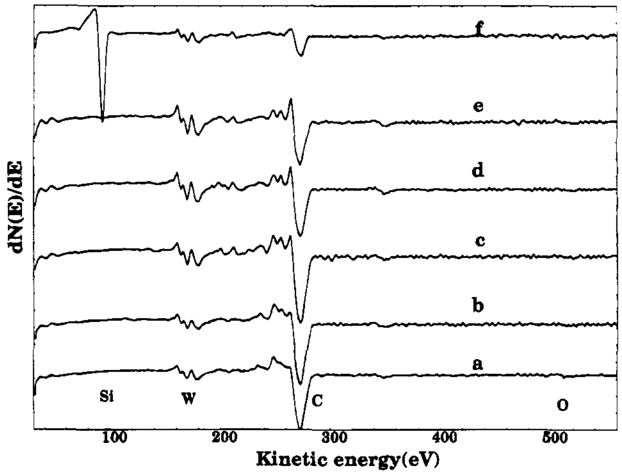

Figure 1. AE spectra of a film deposited from [$HWCp(CO)_3$] at 540 °C and 7.0 mTorr. Cummulative Ar^+ sputtering times: (a) 0, (b) 210, (c) 930, (d) 1530, (e) 3030, and (f) 4530 s.

Continuous films were deposited on Si surfaces which were covered by a thin (~1 nm) photochemical oxide layer. The AES depth profiles of a film deposited on an SiO_2-covered surface at 540 °C and 7 mTorr before and after annealing at 900 °C are shown in Figure 3. The W/C ratio increased with depth in the as-deposited film, reaching a maximum of 0.8 near the buried SiO_2 layer. The oxygen concentration is about 1 at. % in the bulk, equivalent to that of films deposited on Si. The SiO_2 layer is an effective diffusion barrier, as Si does not out-diffuse through the WC film during annealing at 900 °C, as evidenced by Figure 3b. Significantly, annealing resulted in a concentration−depth profile closely similar to that of the as-deposited film on Si (Figure 2a): a carbon-rich surface layer and an underlying region with a W/C ratio of 0.85. Moreover, approximately twice the ion dose was required to sputter through the annealed film as was required for the as-

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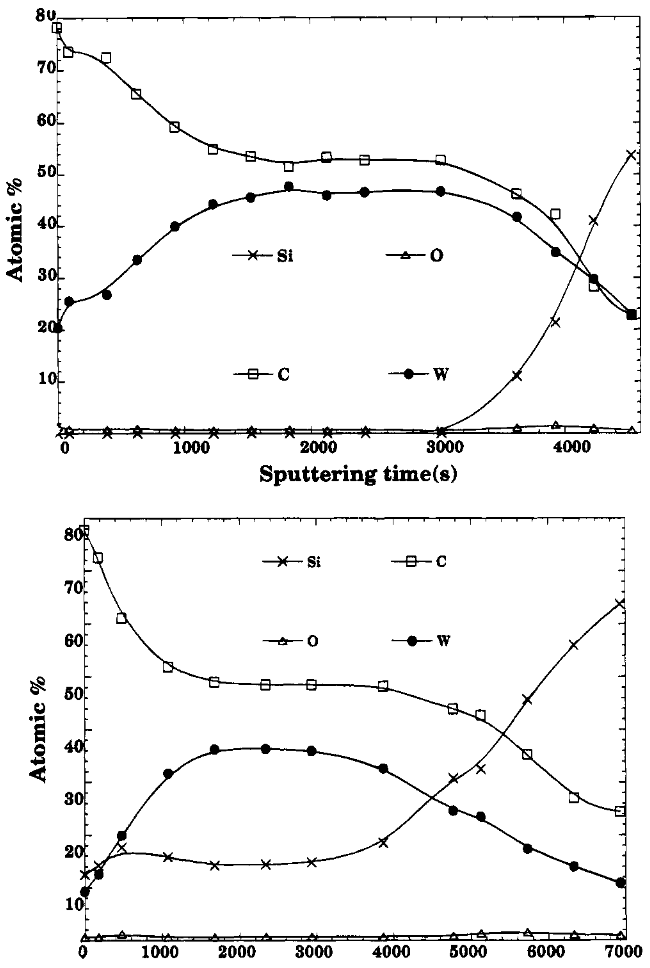

Figure 2. AES composition-depth profile of a film deposited from [HWCp(CO)$_3$] on a Si substrate at 540 °C and 7.0 mTorr: (a, top) as-deposited and (b, bottom) after annealing in vacuo at 900 °C for 20 min.

deposited film, indicating that annealing results in an increase in hardness.

XRD measurements indicate that the films deposited from [HWCp(CO)$_3$] are amorphous. The as-deposited films have very smooth surfaces without the appearance of grains, as revealed by SEM (Figure 4). A typical film deposited in 20 min at 540 °C and 7 mTorr is approximately 3 μm thick. From sheet resistance measurements, we estimate the film resistivity as 4.5×10^{-2} Ω cm.

Owing to its lower vapor pressure, longer deposition times were required to deposit continuous films from [HWCp*(CO)$_3$] than from [HWCp(CO)$_3$] under similar deposition conditions. Films deposited from [HWCp*(CO)$_3$] also have lower W/C ratios (Table 2). The morphology of films deposited from [HWCp*(CO)$_3$] is closely similar to that of films deposited from [HWCp(CO)$_3$].

Cycloheptatrienyl(tricarbonyl)tungsten. Continuous films were deposited from [(cht)W(CO)$_3$] on Si surfaces at 350–700 °C and 1.3 mTorr. The surface carbon concentration increases and the surface oxygen concentration decreases with increasing deposition temperature, as evidenced by AES. At the surface, a mixture of carbidic and graphitic carbon is found for films deposited at 350 °C. In contrast, surface carbon

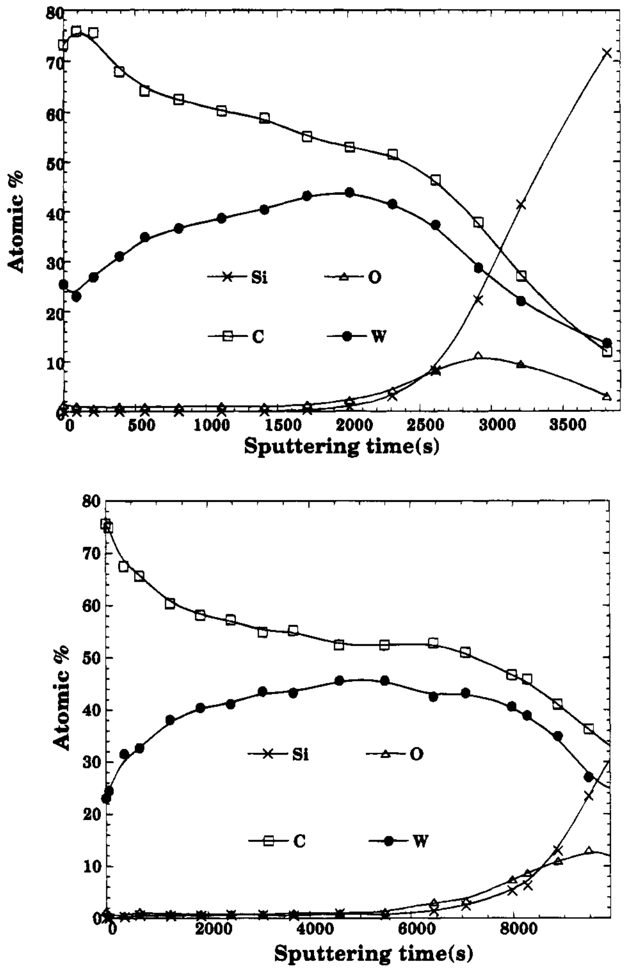

Figure 3. AES composition-depth profile of a film deposited from [HWCp(CO)$_3$] on an SiO$_2$-covered substrate at 540 °C and 7.0 mTorr: (a, top) as-deposited and (b, bottom) after annealing in vacuo at 900 °C for 20 min.

is predominantly graphite for films deposited at 700 °C. The film compositions are given in Table 2.

AES depth profiles, which were measured after the samples were stored in air for several weeks, reveal that the bulk W/C ratios are 1.0 and 0.8 for the films deposited at 350 and 540 °C, respectively. For a film deposited at 350 °C, Figure 5 shows the AE spectra recorded after the indicated Ar$^+$ sputtering times. In the bulk region, the carbon(KLL) line shape is indicative of a mixture of carbidic (major) and graphitic (minor) carbon, except near the Si interface where carbidic carbon is observed. Films deposited from [(cht)W(CO)$_3$] at 540 °C contained more graphitic carbon than those deposited at 350 °C. The depth profile of the film deposited at 540 °C (Figure 6) illustrates the presence of a carbon-rich surface layer and a bulk tungsten carbide region.

SEM (Figure 7) reveals that a typical film deposited on Si from [(cht)W(CO)$_3$] in 1 h at 540 °C and 1.3 mTorr is 60 nm thick with a grain size of about 30–50 nm. The resistivities of these films are about 1 mΩ cm. XRD measurements indicate that the as-deposited films are amorphous.

[(cht)W(CO)$_3$] exhibits intrinsic selectivity for deposition on Si surfaces. AES reveals that after a 1-h exposure of an SiO$_2$-covered surface to [(cht)W(CO)$_3$] vapor, the surface composition is 5 at. % Si and 11 at. % oxygen with about 27 at. % tungsten and 58 at. % carbon.

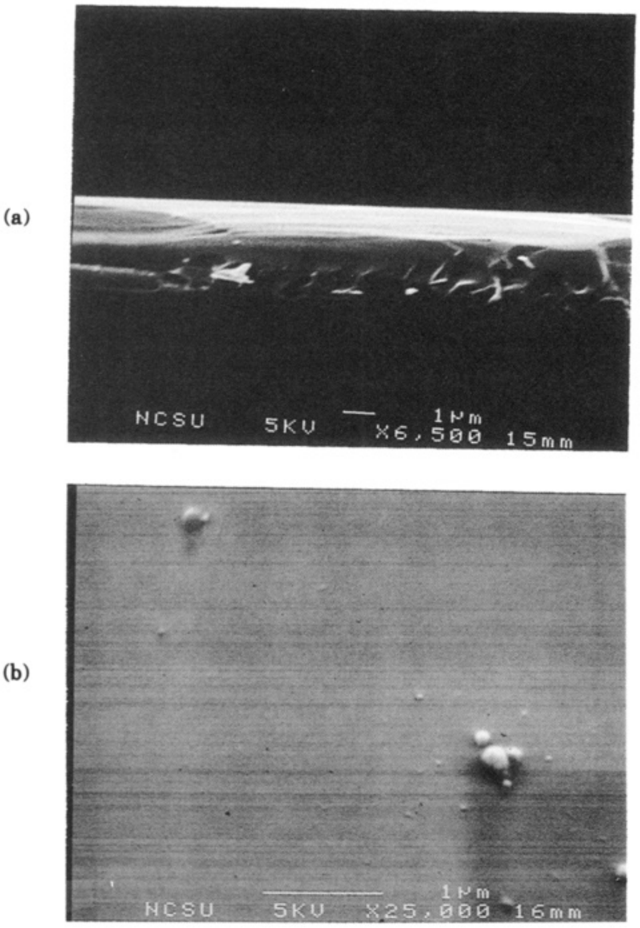

Figure 4. SEM images of a film deposited from [$HWCp(CO)_3$] on a Si substrate at 540 °C and 7 mTorr: (a) cross section; (b) top view.

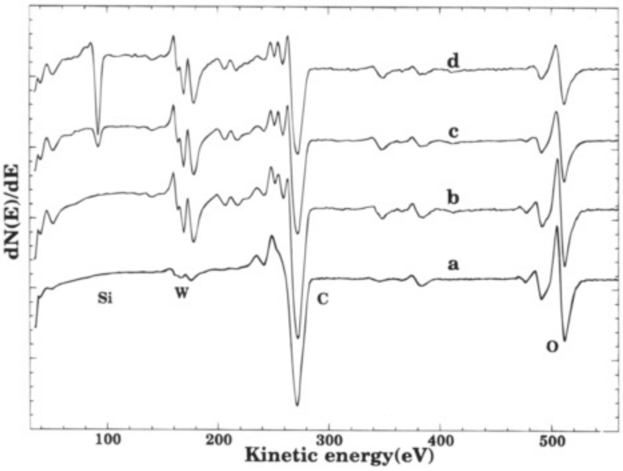

Figure 5. AE spectra of a film deposited from [$(cht)W(CO)_3$] at 350 °C and 1.3 mTorr. Cummulative Ar^+ sputtering times: (a) 0, (b) 30, (c) 60, and (d) 90 s.

Cyclooctadienyl(tetracarbonyl)tungsten. Films deposited by a 1-h exposure to [$(cod)W(CO)_4$] vapor at 400 °C and 3 mTorr are very thin or perhaps discontinuous, as indicated by the Si AES intensity (6.5 at. %). On a Si-free basis, the film contains 45 at. % tungsten, 52 at. % carbon and 3 at. % oxygen. The surface and bulk compositions of a continuous film deposited at 540 °C and 3 mTorr are given in Table 2. The AE spectra in Figure 8, which were recorded after storage in air, reveal the presence of only carbidic carbon throughout the film. Moreover, the film contains less than 1 at. % oxygen. The bulk composition (Table 2) is consistent with a WC_{1-x} phase with $x \simeq 0.46$. The AES depth profile (Figure 9) evidences only a very thin carbon-rich surface layer.

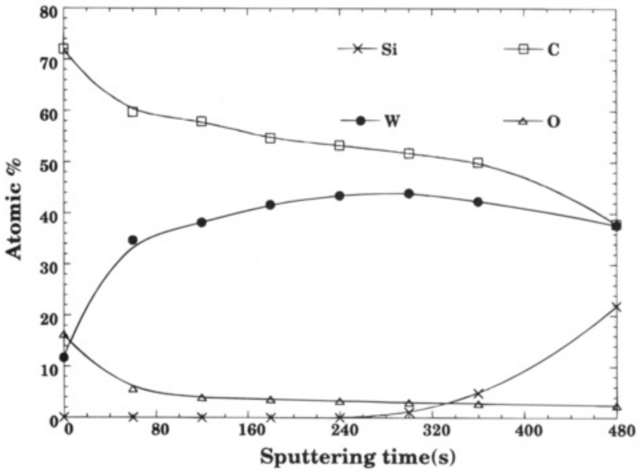

Figure 6. AES composition-depth profile of a film deposited from [$(cht)W(CO)_3$] at 540 °C and 1.3 mTorr.

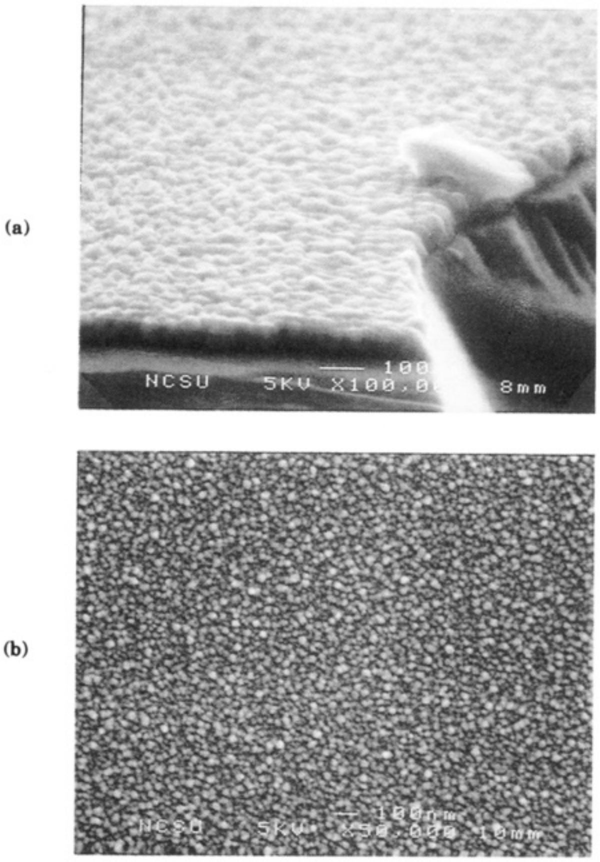

Figure 7. SEM images of a film deposited from [$(cht)W(CO)_3$] at 540 °C and 1.3 mTorr: (a) edge view; (b) top view.

From SEM images (Figure 10) we estimate that the growth rate at 540 °C and 3 mTorr is about 250 nm/h. The grain size of the films is about 100 nm. XRD measurements (Figure 11a) show that these films are amorphous with WC_{1-x} texture. It is not clear if the broad feature between 32° and 44°, on which the WC_{1-x} peaks are superimposed, is due to the amorphous nature of the film or from the Si(100) substrate which also has a broad low-intensity feature at about the same range. The resistivities of these films are approximately 300 $\mu\Omega$ cm.

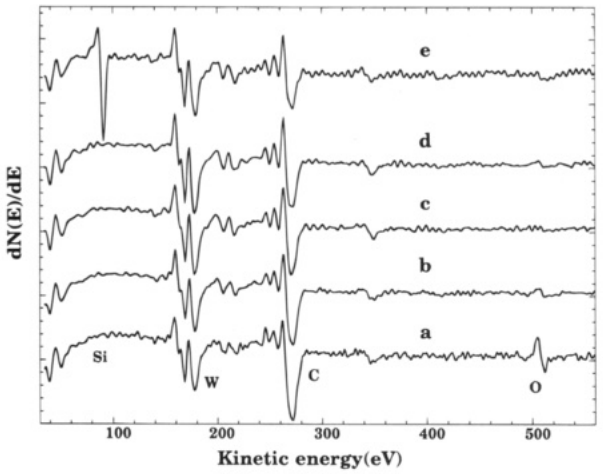

Figure 8. AE spectra of a film deposited from [(cod)W(CO)$_4$] at 540 °C and 3.0 mTorr. Cummulative Ar$^+$ sputtering times: (a) 0, (b) 60, (c) 960, (d) 1320, and (e) 3000 s.

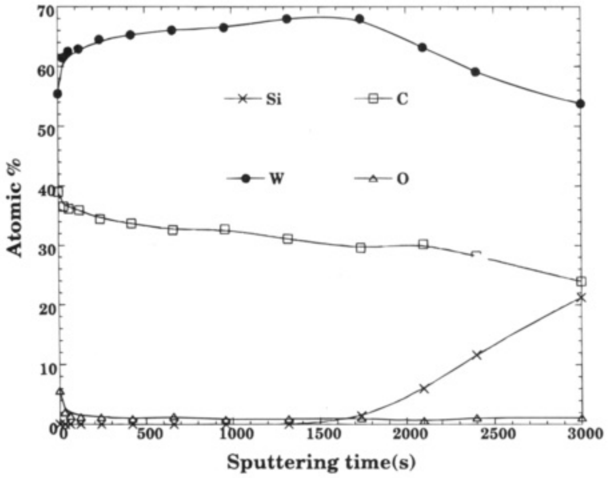

Figure 9. AES composition-depth profile of a film deposited from [(cod)W(CO)$_4$] at 540 °C and 3.0 mTorr.

Toluene(tricarbonyl)tungsten. The reported decomposition temperature of [(toluene)W(CO)$_3$] is 139–142 °C;[14] however, it was observed that [(toluene)W(CO)$_3$] decomposed in the source tube at about 100 °C resulting in a dark brown deposit. Consequently, a source temperature of 90 °C was used for LPCVD. Substrate temperatures in excess of 400 °C are required for deposition of continuous films at 7.5 mTorr with a 1-h deposition time.

AE spectra of a film deposited from [(toluene)W(CO)$_3$] at 540 °C and 7.5 mTorr, which were measured after the indicated Ar$^+$ sputtering times, are shown in Figure 12; the corresponding depth profile is given in Figure 13. The bulk composition is uniform, and there is only a very thin carbon- and oxygen-rich surface layer. The AES carbon(KLL) line shape indicates that carbon is present in the carbidic form at the surface and throughout the film. The surface and bulk compositions of the as-deposited film are given in Table 2. The bulk composition is consistent with a WC$_{1-x}$ phase with $x \simeq 0.69$; however, the bulk oxygen content is high, ~5 at. %. XRD measurements reveal α-W$_2$C texture in the as-deposited film as evidenced by the broad low-intensity peak in Figure 11b.

The average growth rate of the films deposited from [(toluene)W(CO)$_3$] at 540 °C and 7.5 mTorr is about 360 nm/h, and the grain size is about 30 nm, as indicated by SEM images (Figure 14). From four-point probe

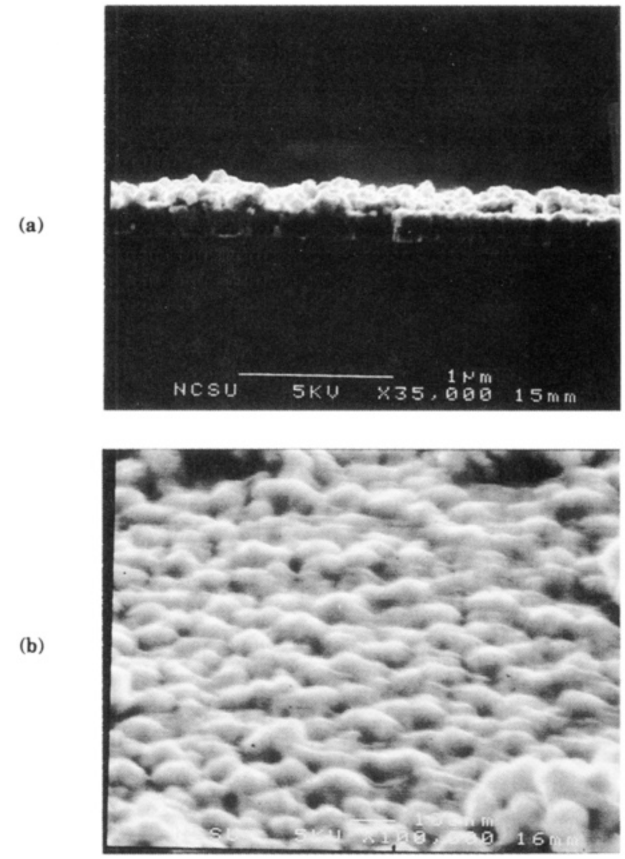

Figure 10. SEM images of a film deposited from [(cod)W(CO)$_4$] at 540 °C and 3.0 mTorr: (a) cross section; (b) top view.

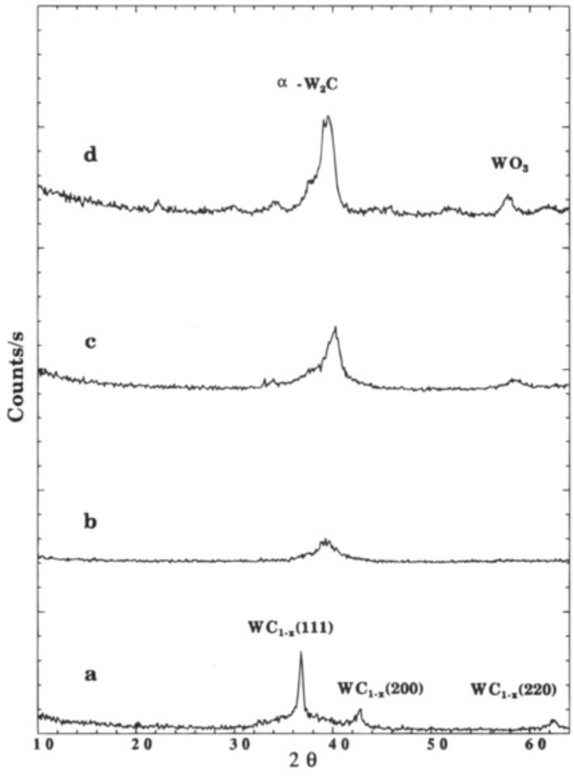

Figure 11. XRD patterns: (a) film deposited from [(cod)W(CO)$_4$] at 540 °C and 3 mTorr; (b) film deposited from [(toluene)W(CO)$_3$] at 540 °C and 7.5 mTorr; (c) film deposited from [(toluene)W(CO)$_3$] at 600 °C and 7.5 mTorr; and (d) film of (c) after annealing in vacuo at 900 °C.

Table 3. Summary of Results: Tungsten Carbide OMCVD at 540 °C

source compound	grain size (nm)	deposition rate (nm/h)	resistivity ($\mu\Omega$ cm)	crystallinity	W/C ratio	AES C(KLL) line shape, surface/bulk
$HWCp(CO)_3$	smooth			amorphous	0.9	graphitic/mixture
$(cht)W(CO)_3$	30−50	60	1000	amorphous	0.8	graphitic/mixture
$(cod)W(CO)_4$	100	250	380	amorphous with WC_{1-x} texture	1.9	mixture/carbidic
$(toluene)W(CO)_3$	30	360	280	amorphous with W_2C texture	3.2	carbidic/carbidic

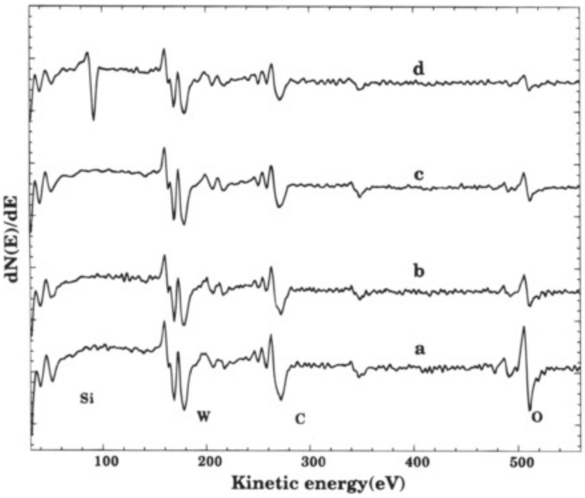

Figure 12. AE spectra of a film deposited from [$(toluene)W(CO)_3$] at 540 °C and 7.5 mTorr. Cummulative Ar^+ sputtering times: (a) 0, (b) 60, (c) 430, and (d) 1330 s.

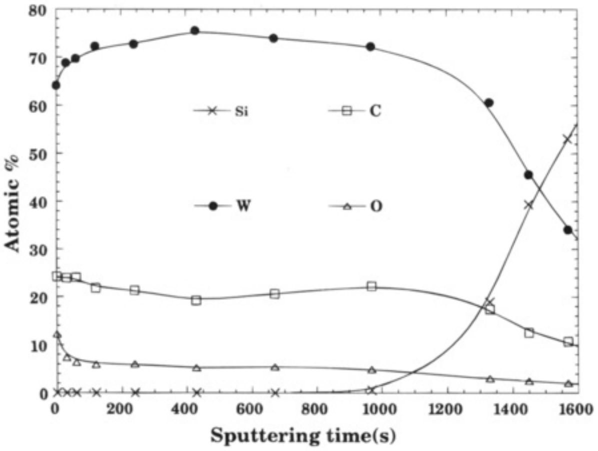

Figure 13. AES composition-depth profile of a film deposited from [$(toluene)W(CO)_3$] at 540 °C and 7.5 mTorr.

measurements, we estimate the resistivity of these films as 280 $\mu\Omega$ cm.

Films deposited from [$(toluene)W(CO)_3$] at 600 °C contain slightly less tungsten (60−70 at. %) with about 25−30 at. % carbon and about 10 at. % oxygen. In addition to the α-W_2C texture, XRD measurements (Figure 11c) indicate the presence of WO_3 precipitates, consistent with the higher oxygen content. After annealing at 900 °C, the bulk tungsten concentration increases to greater than 70 at. % with less than 5 at. % oxygen and about 20 at. % carbon. Out-diffusion and surface segregation of Si also occurred during annealing. After annealing, the peak assigned to α-W_2C is intensified, and the peak assigned to tungsten oxide is shifted slightly to lower 2θ values (Figure 11d).

Discussion

The tungsten carbide films reported here span a much broader range of W/C stoichiometries (Table 3) than those previously deposited by OMCVD; significantly, the films contain less oxygen than films deposited by other workers from all-hydrocarbon W complexes (Table 2). The present data are expected to closely reflect the intrinsic deposition chemistry of the source compounds, due to careful exclusion of water and oxygen from the growth environment and in situ off-line thin-film analysis. The films deposited from [$HWCp(CO)_3$] and [$(cht)W(CO)_3$] are amorphous WC incorporating excess graphitic carbon and are similar (except in oxygen content) to those deposited from [$(Me_3CCH_2)_3W{\equiv}CCMe_3$] and [$W(\eta^3$-$C_3H_5)_4$] by Xue et al.[10] and Kirss et al.,[11] respectively. In contrast, the films deposited from [$(cod)W(CO)_4$] and [$(toluene)W(CO)_3$] are W-rich and exhibit crystalline texture.

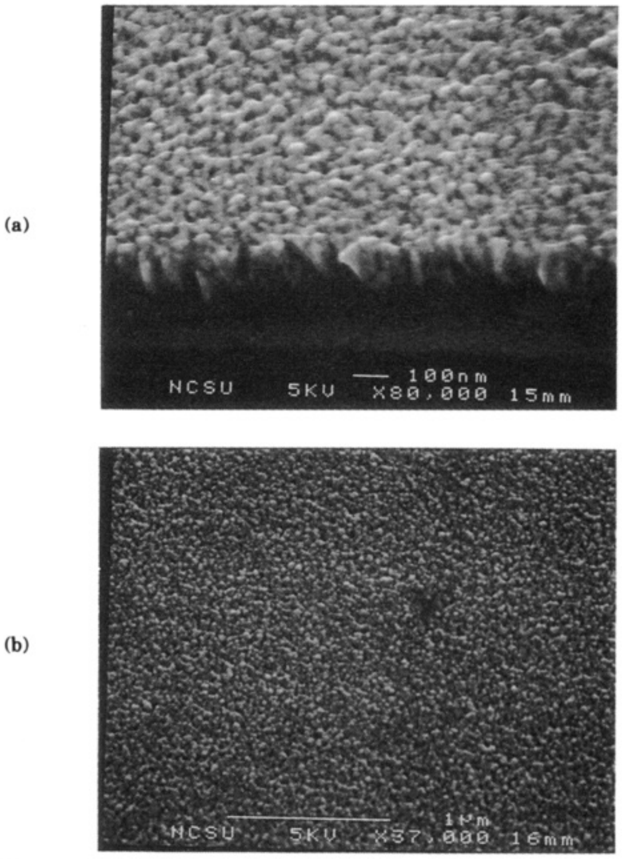

Figure 14. SEM images of a film deposited from [$(toluene)W(CO)_3$] at 540 °C and 7.5 mTorr: (a) cross section; (b) top view.

The tungsten carbide deposition rate increases with reactor operating pressure, which in these experiments was established by the source-compound vapor pressure at the temperature listed in Table 1. At 90 °C, [$HWCp(CO)_3$] and [$(toluene)W(CO)_3$] are approximately 1 order of magnitude less volatile than [$W(CO)_6$]. The vapor pressures of the other tungsten carbonyl derivatives are even lower, necessitating source temperatures in excess of 100 °C to achieve measurable growth rates. [$HWCp(CO)_3$] exhibited the highest gross deposition rate, but this datum is not included in Table 3, due to the uncertain thickness of the graphitic overlayer. The electrical resistivity of the films decreases with increasing tungsten content. For comparison, the resistivities of bulk WC and W_2C are 25 and 80 $\mu\Omega$ cm, respectively, at 25 °C.[5b] The very high apparent resistivities of films deposited from [$HWCp(CO)_3$] are likely due to the graphitic overlayer. The films deposited from [$(cht)W(CO)_3$] and [$(toluene)W(CO)_3$] exhibit similar grain sizes; films deposited from [$(cod)W(CO)_4$] contain larger 100-nm grains.

The thin-film compositions can be rationalized by considering the molecular structures and thermochemistries of the precursors. The W−ligand (W−L) bond energies listed in Table 4 were derived from the heats of formation of the reference compounds. The relatively small W−CO bond energy suggests that CO ligands will be dissociated initially on thermolysis of each complex. CO disproportionation leading to CO_2 and deposited carbon is thermodynamically favorable under the deposition conditions; however, on-line gas analysis during W OMCVD from [$W(CO)_6$] evidenced that CO is the predominant reaction byproduct.[33] Consequently, the hydrocarbon ligands are believed to be the primary sources of carbon atoms in the films. Consistent with this hypothesis, an isotopic labeling study of the vapor decomposition of [$(cht)Cr(CO)_3$] demonstrated that more than 87% of the carbon in the deposited chromium carbide films could be attributed to the cht ligand.[34] (Cr−CO and Cr−cht have bond energies of 108 and 150 kJ/mol, respectively.[26]) Neutral hydrocarbon ligands (e.g., toluene, cod, and cht) are more likely to desorb as intact molecules than metal-bound hydrocarbon fragments bearing a formal negative charge (e.g., CH_3, Cp, and Cp*). The latter moieties are expected to either react intramolecularly via C−H activation (e.g., α-hydride transfer) forming strong metal−carbon bonds[10,11] or desorb as radical species via homolytic bond cleavage.[35] With these expectations in mind, the OMCVD results for each precursor are discussed below.

Films deposited from [$HWCp(CO)_3$] at 540 °C have W/C ratios of ~0.9 and contain less than 1 at. % oxygen; however, the tungsten carbide is covered by a thick graphitic overlayer. The required deposition temperature is much greater than the 180 °C decomposition temperature of [$HWCp(CO)_3$],[14−16] which attests to the thermal stability of the WCp moiety. The initial decomposition products contain excess carbon and require high-temperature pyrolysis to convert them to WC. This process involves hydrogen transfer with the concomitant formation of WC, volatile hydrocarbon products, and graphite. Similar chemistry has been reported for [$VCp(CO)_4$]: decomposition of [$VCp(CO)_4$] at 350 °C on quartz results in a carbon-rich deposit (C/V = 2.75), which is converted on annealing at 700 °C to V_4C_3 incorporating excess carbon.[36] Comparison of the results from [$HWCp(CO)_3$] and [$HWCp^*(CO)_3$] indicates that the replacement of all Cp hydrogen atoms with methyl groups does not significantly alter the deposition chemistry. This can be rationalized, since the Cp* ligand contains more carbon atoms but has a higher H/C ratio.

Table 4. W−Ligand Bond Energies

ligand	formal charge	bond energy contribution (kJ/mole)	model compound	ref
CH_3	−1	159−160	$W(CH_3)_6$	26, 27
CO	0	180	$W(CO)_6$	26
cyclooctadiene	0	~200[a]		
benzene	0	298	$W(benzene)_2$	28, 29
toluene	0	304 ± 6	$W(toluene)_2$	29, 30
H	−1	305−311	Cp_2WH_2	29, 31
		302	$HCpW(CO)_3$	29
cycloheptatriene	0	311	$(cht)W(CO)_3$	26
mesitylene	0	339 ± 16	$(mesitylene)W(CO)_3$	30
Cl	−1	347	WCl_6	26
η^5-C_5H_5	−1	447	H_2WCp_2	28
η^5-$C_5(CH_3)_5$	−1	>447		28, 32
F	−1	508	WF_6	26

[a] Estimated on the basis of the number of π-bound olefin groups.

In contrast, [$CH_3WCp(CO)_3$] is reported to be the precursor of β-W films containing only 5−15% carbon (Table 2).[12] The markedly different results obtained by substitution of CH_3 for H can be understood by considering the respective W−L bond energies, which provide conservative estimates of the activation energies for homolytic bond cleavage. Since the W−CH_3 bond energy is much less than the W−H bond energy, methyl radical formation is predicted to be facile relative to hydrogen radical formation. The resultant methyl radical might then react with the Cp ligand forming volatile CpMe, substantially reducing carbon incorporation into the growing film. Similar radical-mediated chemistry has been proposed to explain the deposition of high-purity Pd thin films from [$Pd(\eta^3$-$C_3H_5)_2$].[35]

Films deposited from [$(cht)W(CO)_3$] at 540 °C have W/C ratios closely similar to those of films deposited from [$HWCp(CO)_3$], but they are not covered by a thick graphitic overlayer. Significantly, continuous WC films can be deposited from [$(cht)W(CO)_3$] at lower temperatures, e.g., 350 °C. These films are nearly stoichiometric WC, and the C(KLL) AES line shape is consistent with predominantly carbidic carbon. On the basis of the chemistry reported for [$(cht)Cr(CO)_3$],[34] the cht ligand is the most probable carbon source.

[$(cod)W(CO)_4$] is perhaps the most promising of the precursors investigated in this study. The cod ligand is weakly bonded to the W center with an estimated bond energy comparable to that of W−CO (Table 4). This should result in facile ligand dissociation on thermolysis and a reduced propensity for graphite formation. Unfortunately, [$(cod)W(CO)_4$] has a low vapor pressure, and a growth rate of only 0.3 μm/h is obtained at 540 °C and 3.0 mTorr. Amorphous tungsten carbide films with WC_{1-x} crystalline texture are deposited under these conditions; the films contain little if any graphitic carbon and less than 1 at. % oxygen. WC_{1-x} is a nonstoichiometric carbide phase with a variable composition: $0.33 \le x \le 0.4$, which exists in equilibrium only at temperatures greater than or equal

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to 2530 °C.[5] The AES-determined film composition ($x = 0.46$) is slightly outside this range. This could result from compositional inhomogeneity within the film or systematic errors in the elemental analysis. Interestingly, these thin WC_{1-x} films are not oxidized by prolonged air exposure.

Films deposited from [(toluene)$W(CO)_3$] at 540 °C and 7.5 mTorr are amorphous tungsten carbide with weak W_2C crystalline texture. Anomalously, the films contain approximately 5 at. % oxygen—more than films deposited at 540 °C from [$W(CO)_6$][13] and the other W carbonyl derivatives. The W_2C texture is enhanced by deposition at 600 °C and by postdeposition annealing at 900 °C. The films contain >70 at. % W, but XRD peaks of crystalline W phases are not observed (Figure 11b–d). The W content is much greater than that of films deposited from [(cht)$W(CO)_3$], although the precursors have the same empirical formula and the W–toluene and W–cht bond energies are nearly equal (Table 4). The aromatic stability of the toluene ligand is apparently important, since bis-arene tungsten compounds (e.g., [(benzene)$_2$W]) are reported as precursors of high-purity W films.[37,38]

Conclusions

[$HWCp(CO)_3$], [$HWCp^*(CO)_3$], and [(cht)$W(CO)_3$] are precursors of amorphous WC films containing excess graphitic carbon. Dehydrogenation of the strongly bound Cp, Cp*, and cht ligands is suggested to be the source of carbon in these films. In contrast, [(cod)$W(CO)_4$] and [(toluene)$W(CO)_3$] are precursors of tungsten-rich films with WC_{1-x} and W_2C crystalline textures, respectively. Notwithstanding the presence of carbonyl oxygen in the precursors, the films deposited at 540 °C contain only 1 at. % oxygen or less (with the exception of films derived from [(toluene)$W(CO)_3$] which contain 5 at. % oxygen). [(cht)$W(CO)_3$], [(cod)$W(CO)_4$], and [(toluene)$W(CO)_3$] are useful single-source precursors for tungsten carbide LPCVD; the choice depends on the desired film composition.

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