

Chemical Vapor Deposition of Tungsten Oxide

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Crystalline and amorphous thin films of tungsten(VI) oxide can be prepared by chemical vapor deposition using a variety of volatile precursors below 500 °C. Deposition parameters for preparation of WO₃ films from tungsten hexacarbonyl [W(CO)₆], tungsten hexafluoride (WF₆), tungsten ethoxides [W(OEt)_x, x = 5, 6] and tetra(allyl)tungsten [W(η³-C₃H₅)₄] are summarized. The electrochromic behavior of these films is comparable with that observed for WO₃ films prepared by evaporation, sputtering and electrodeposition. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The electrochromic behavior of tungsten(VI) oxide makes WO₃ an attractive material for electronic devices.¹ Partial reduction of colorless WO₃ generates an intense blue color assigned to intervalence charge transfer in partially reduced WO₃. The electrochemical reduction of tungsten(VI) to tungsten(V) is accompanied by uptake of cations (e.g. H⁺, Li⁺ etc.) to maintain electrical neutrality, and is reversible. Applications for thin films of WO₃ and other electrochromic materials include 'smart windows', electrochromic displays and other electronic devices.¹

Both amorphous and crystalline tungsten oxide films have been prepared. The electrochromic properties are strongly dependent on the preparative method and conditions. For example, sol-gel-derived WO₃ films do not exhibit electrochromism unless they are annealed or laser-fired.² The early

literature contains several reports of electro-optically inactive WO₃ films prepared by sputtering, evaporation or spray methods,³ although later work has yielded electrochromic WO₃ films by these methods.¹ No attempt is made here to review the literature pertaining to WO₃ films prepared by these methods.

The present review focuses on CVD of amorphous and crystalline tungsten oxide films, including thermal CVD, plasma-enhanced CVD (PECVD) and photo-assisted CVD (PACVD). The principle advantage of chemical vapor deposition of electronic materials over other methods is in step coverage, the absence of radiation damage, throughput and the possibility for selective growth.⁴ For example, CVD of WO₃ occurs at temperatures significantly below those for evaporation (1300 °C).⁵

FILM GROWTH

CVD of WO₃ from tungsten hexafluoride (WF₆) and tungsten carbonyl [W(CO)₆] precursors has received the greatest attention. Both compounds are volatile and commercially available. Tungsten trioxide films have also been prepared from tungsten alkoxides, W(OC₂H₅)_n (n = 5, 6). Recently, we have prepared thin films of WO₃ from tetra(allyl)tungsten, W(η³-C₃H₅)₄. A summary of deposition conditions and film composition is to be found in Table 1.

TUNGSTEN HEXAFLUORIDE

Tungsten hexafluoride, WF₆, is widely applied as a precursor for the deposition of tungsten metal and has been used in the deposition of tungsten oxides.^{4,6} Deposition of pure tungsten from WF₆ under H₂ or SiH₄ results in inclusion of some crystalline W₂₀O₅₈ and possibly other tungsten oxide impurities in body-centered cubic (bcc) tungsten films.⁷

Tungsten oxide films have been intentionally

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Table 1 Comparison of film deposition conditions and composition

Precursor	Growth temp. (°C)	Growth rate (nm/min)	Film thickness	Structure	O:W ratio	Ref.
W(CO) ₆ /O ₂ anneal	500	— ^a	185–1500	Crystalline	3:1	15–17
W(CO) ₆ /O ₂ /O ₂ anneal	500	— ^a	185–1500	Crystalline	3.12:1	15–17
W(CO) ₆ /air	200–400	30–40	250	Amorphous	1.83:1	21–24
W(CO) ₆ /air/hv	150–250	200–400	250	Amorphous	2.92:1	25
W(CO) ₆ /O ₂ (PECVD)	60	8–9		Amorphous		10
WF ₆ /O ₂ (PECVD)	50–60	28	150–650	Amorphous	3.7:1	10
WF ₆ /H ₂ /air	50–60	18–24	250		≈ 3:1	11
W(OEt) _x (X = 5, 6)	100–300	0.75–30		Amorphous	2.6–3.2:1	6
W(allyl) ₄ /O ₂ anneal	250–450	— ^a	250	Crystalline		32

^a For these samples, the oxide is generated by oxygen annealing of a previously prepared WO_xC_y film, so direct comparisons of growth rates are meaningless.

deposited from WF₆ using pure oxygen or air. A growth rate of 28 nm min⁻¹ was reported for an amorphous WO₃ grown from WF₆ in air using plasma-enhanced CVD.^{8,9} Films ranging from 150 to 650 nm in thickness were deposited at low substrate temperature (50–60 °C) on indium tin oxide-coated sodalime glass substrates. Analysis of fluorine-free films prepared in this fashion gave an O/W ratio of 3.7:1 by Auger spectroscopy.

WO₃ films have also been grown on a wide variety of substrates from WF₆ and room air in the presence of radiofrequency-generated hydrogen atoms.¹⁰ Growth rates ranged from 18 to 24 nm min⁻¹ producing amorphous, producing films 250 nm thick with a 3:1 ratio of oxygen to tungsten. Fluorine impurities were not detected in these films, but fluorine-doped WO₃ films can be prepared from pyrolysis of WF₆ in the presence of difluoroethane and isopropanol as the fluorine and oxygen sources.¹¹

TUNGSTEN HEXACARBONYL

Thermal decomposition of W(CO)₆ above 400 °C in the absence of oxygen produces tungsten metal contaminated with carbon and oxygen.^{12–14} As-deposited films of this type have been referred to as 'reflective tungsten' to distinguish them from 'black tungsten' films deposited from W(CO)₆ in the presence of oxygen under the same conditions. X-ray diffraction (XRD) and Reflection High Energy Electron Diffraction (RHEED) data on black tungsten films were consistent with W₁₈O₄₉ and either tetragonal WO_{2.9} or monoclinic W₂₀O₅₈.¹¹ X-ray photo-electron spectroscopy (XPS) confirmed the presence of tungsten(V) and

tungsten(VI) in 'black tungsten' films. Films were successfully deposited on quartz, aluminum, and tin oxide-coated glass.

XRD, RHEED and XPS data for 'black' or 'reflective' tungsten films annealed in oxygen between 400 and 600 °C were consistent with formation of polycrystalline WO₃ containing monoclinic WO₃.¹² The oxygen tungsten ratio in the transparent films ranged from 2.77:1 to 3.57:1, depending on annealing temperature and the partial pressure of oxygen.¹⁵ Oxidation rates ranged from 1 to 2 nm min⁻¹ producing films from 185 to 1500 nm thick.^{16,17}

Decomposition of W(CO)₆ in air between 200 and 400 °C produces amorphous, transparent WO₃ films with O/W ≈ 1.83:1. The films contain metal and grow at a rate of 30–40 nm min⁻¹.^{18–24} Growth temperatures were further reduced to ≈ 150 °C and growth rates (200–400 nm min⁻¹) were significantly enhanced using photo-assisted CVD (PACVD).^{21–24} The oxygen/tungsten ratio in the PACVD films (≈ 250 nm thick) increased to ≈ 2.92:1. Growth rates for plasma-enhanced CVD using W(CO)₆ in O₂ at 60 °C are in the range of 8–9 nm min⁻¹.¹⁰

TUNGSTEN ALKOXIDES

Tungsten alkoxydes are attractive precursors for CVD of tungsten oxide thin films avoiding, in principle, the need for oxygen annealing steps. There is one report of CVD of tungsten oxide using tungsten ethoxides, W(OC₂H₅)_n (n = 5, 6).²⁵ Pentakis(ethoxy)tungsten is a volatile liquid and hexakis(ethoxy)tungsten is a solid. Amorphous, adherent films of WO₃ (O:W ratio 2.7–3.2:1) were

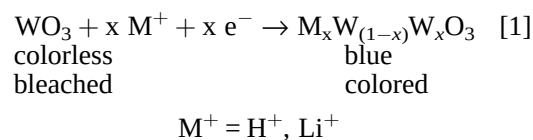
Table 2 Summary of electrochromic properties of CVD WO₃ films

Deposition method	Precursor	Structure	n ^a (cm ² C ⁻¹)	Response time		Ref.
				Coloration	Bleaching	
Thermal CVD	W(CO) ₆	Amorphous	230	30 s	30 min	18–20
	W(CO) ₆	Crystalline	40 ^b	0.330 s	13 s	13,14
			25.5	60–120 s		13–16
			n.r. ^c	n.r.	n.r.	25
	W(OEt) _x	Amorphous	n.r.	n.r.	n.r.	31
PACVD	W(allyl) ₄	Crystalline	n.r.	2 min	10 min	21–24
PECVD	W(CO) ₆	Amorphous	222	30 s		8,9
	WF ₆	Amorphous	100			

^a In 1M LiClO₄ or LiBF₄ unless otherwise noted. ^b 1M H₂SO₄. ^c n.r., not reported.

grown on quartz, sodalime glass, indium tin oxide-coated glass and silicon. Growth rates ranged from 0.75 to 30 nm min⁻¹ over the temperature range 100–300 °C. Carbon contamination was below 2 atom%. Powdery blue films were deposited above 350 °C.

for application in electrochromic devices can be assessed through measurement of several parameters, including coloration efficiency, response time and cycle life^{1,32} The electrochromic properties of CVD WO₃ films are summarized in Table 2. The color change is described by Eq. [1] and in Fig. 1:



ORGANOMETALLIC TUNGSTEN COMPOUNDS

A number of organometallic tungsten compounds have been investigated as precursors for the CVD of tungsten metal,⁶ including bis(cyclopentadienyl)-tungsten dihydride, [(η⁵-Cp)₂WH₂]²⁶ tris(methylvinylketone)tungsten, [W(C₄H₆O)₃],²⁷ tris(butadiene)tungsten [W(C₄H₈)₃]²⁷ and tetra(allyl)tungsten, [W(η³-C₃H₅)₄].²⁸ Tungsten carbide films have been grown from CpW(CO)₃H, Cp*W(CO)₃H, (C₇H₈)W(CO)₃, (C₈H₁₂W(CO)₃, toluene-W(CO)₃,²⁹ and Me₃C(CH₂)₂W≡CCMe₃.³⁰ Deposition of tungsten oxide films from these precursors has not been reported.

Dark, reflective films (250 nm thick) deposited from $W(\eta^3\text{-C}_3\text{H}_5)_4$ under vacuum contain both carbon and oxygen (WC_xO_y ; $X \approx 1$, $Y \approx 0.25$ by XPS).²⁸ These amorphous films turn blue in air over a period of days to weeks depending on the film thickness.³¹ Annealing under oxygen at 400 °C produces transparent, colorless films containing crystalline WO_3 (by XRD) but retaining significant amounts of carbon (17 atom%).

OPTICAL AND ELECTROCHROMIC PROPERTIES

The quality of CVD-prepared tungsten oxide films

COLORATION EFFICIENCY

The coloration efficiency, η , of an electrochromic thin film is determined from Eq. [2], where α is the absorption coefficient, d the film thickness, ΔA the change in optical absorption and Q the charge

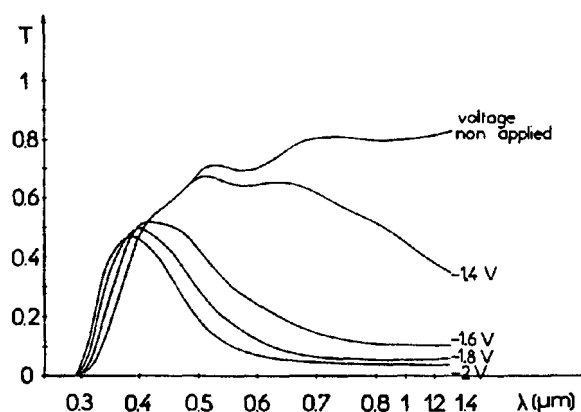


Figure 1 UV–Vis spectrum of WO_3 as a function of applied voltage.¹³

injected per unit area. A large coloration efficiency is desirable for electronic display and window applications. The coloration efficiency depends on the film growth conditions and on the precursor.

$$\eta \frac{(\alpha d)}{Q} = \frac{\Delta A}{Q} \quad [2]$$

Amorphous WO₃ thin films prepared by PACVD from W(CO)₆ can have coloration efficiencies similar to those prepared by thermal CVD. Crystalline WO₃ films prepared by thermal CVD from W(CO)₆, however, have η values more than five times less than the amorphous films. Amorphous WO₃ films prepared by plasma-enhanced CVD using WF₆ had coloration efficiencies of 100 cm² C⁻¹, between the values for amorphous and crystalline films prepared using W(CO)₆. There are no data on coloration efficiencies of films deposited from tungsten alkoxides or other organo-metallic precursors. Coloration efficiency is also dependent on the electrolyte, i.e. LiClO₄ or H₂SO₄.

RESPONSE TIME

The elapsed time for conversion of WO₃ from a colored, reduced form to the 'bleached', oxidized form (or vice versa) is called the response time. A response time of the order of seconds or minutes is acceptable for electrochromic windows but much faster response times are required for displays. A direct comparison of response time values is difficult as different criteria are employed in the measurement. Electrochromic WO₃ films prepared by CVD generally color faster than they are bleached. The shortest coloration times are of the order of 0.33 seconds to achieve measureable decreases in transmission (increases in absorption) in the visible region of the spectrum.^{13,14} The bleaching times show a far greater range, requiring up to 30 min for complete decoloration in some cases.

CYCLE LIFE

The cycle life of an electrochromic film reflects the number of coloration/bleaching cycles a particular film can tolerate before a noticeable loss or failure in performance is observed. Longer cycle lives are

desirable for any device applications. Limited data on cycle life for CVD WO₃ films have been reported, but they appear to be stable for tens of cycles.

DISCUSSION

Tungsten trioxide films have been prepared by chemical vapor deposition using a variety of tungsten precursors. By comparison with other deposition methods, CVD-prepared films have similar electrical and optical characteristics.

Electrochemically deposited WO₃ films with response times of ≈ 0.1 s have been reported.³³ WO₃ films sputtered from the metal oxide have response times measured in seconds, but recent results³⁴ show a strong dependence of the electrochromic properties on preparation methods. WO₃ films sputtered from the metal in an oxidizing atmosphere have longer response times, ranging from less than 30 s for coloring to more than 1 min for bleaching. These data are similar to the range of results observed for CVD films using W(CO)₆ as a precursor. Sol-gel-derived films have coloration times of 120 s.³ There is some evidence that response time is a function of film density.³² The electrochemically deposited films with the fastest response times have densities between 4.8 and 5.0 g cm⁻³ compared with 5.3–6.5 g cm⁻³ for vacuum-evaporated films and 5.62 g cm⁻³ for CVD films prepared using tungsten hexacarbonyl.^{13–17} Bulk WO₃ has a density of 7.16 g cm⁻³.

The coloration efficiencies for CVD WO₃ films are generally comparable and are sometimes better than films prepared by other deposition techniques. For example, amorphous WO₃ films prepared by thermal evaporation have η values ranging from 76 to 115 cm² C⁻¹ compared with a value of 222 cm² C⁻¹ for amorphous CVD films. Polycrystalline films grown by dc (direct current) or radio-frequency sputtering have η values ranging from 42 to 115 cm² C⁻¹, compared to η values between 26 and 41 cm² C⁻¹ for crystalline WO₃ films prepared by CVD.

Our knowledge of the effect of the precursor on electrochromic properties is hampered by an absence of data on coloration efficiency and response times for all the precursors. Data on WF₆ and W(CO)₆ indicate similar electrochromic behavior for films grown from either precursor (Table 2). The electrochromic properties, however,

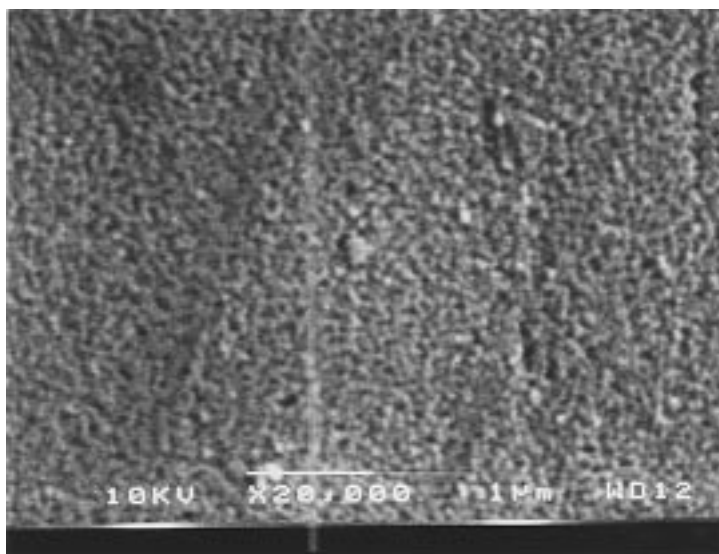


Figure 2 SEM of WO₃ film grown from W(η^3 -C₃H₅)₄.

are clearly dependent on growth conditions and film crystallinity.

Smooth, adherent and uniform films have been grown using all four precursors cited in Table 2 (Fig. 2). The microstructure of the films is dependent on substrate and deposition conditions. MOCVD using W(CO)₆ on borosilicate glass produced smooth featureless films, whereas films deposited on fluorine-doped tin oxide were coarse and dull in appearance.²⁵ Changing deposition conditions for W(OEt)₅ and WF₆ results in powdery, non-adherent films.^{6,10}

CONCLUSIONS

The deposition of electrochromic tungsten(VI) oxide films by CVD has received little attention in comparison with other thin-film growth methods. A survey of the literature suggests that the coloration efficiency of CVD WO₃ films is comparable with that of those prepared by evaporation, electrodeposition or sputtering. Response times are adequate for application in 'smart window' technology. Unfortunately, the films with the best coloration efficiency and deposited at the fastest growth rates do not coincide with the shortest response time. Investigations of alternative precursors to WO₃ which combine rapid growth with short response times at high color efficiencies

appear to be warranted although widespread application of CVD WO₃ films in large-area devices such as window coatings may not be competitive with sol-gel or electrodeposition techniques.

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