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 WO_3 films from tungsten hexacarbonyl [$W(CO)_6$], tungsten hexafluoride (WF_6), tungsten ethoxides [$W(OEt)_x$, $x = 5$, 6] and tetra(allyl)tungsten [$W(\eta^3\text{-}C_3H_5)_4$] are summarized. The electrochromic behavior of these films is comparable with that observed for WO_3 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 WO_3 an attractive material for electronic devices.[1] Partial reduction of colorless WO_3 generates an intense blue color assigned to intervalence charge transfer in partially reduced WO_3. 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 WO_3 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 WO_3 films do not exhibit electrochromism unless they are annealed or laser-fired.[2] The early literature contains several reports of electro-optically inactive WO_3 films prepared by sputtering, evaporation or spray methods,[3] although later work has yielded electrochromic WO_3 films by these methods.[1] No attempt is made here to review the literature pertaining to WO_3 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 WO_3 occurs at temperatures significantly below those for evaporation (1300 °C).[5]

FILM GROWTH

CVD of WO_3 from tungsten hexafluoride (WF_6) 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, $W(OC_2H_5)_n$ ($n = 5$, 6). Recently, we have prepared thin films of WO_3 from tetra(allyl)tungsten, $W(\eta^3\text{-}C_3H_5)_4$. A summary of deposition conditions and film composition is to be found in Table 1.

TUNGSTEN HEXAFLUORIDE

Tungsten hexafluoride, WF_6, 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 WF_6 under H_2 or SiH_4 results in inclusion of some crystalline $W_{20}O_{58}$ 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/$h\nu$	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·/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 WF_6 using pure oxygen or air. A growth rate of 28 nm min^{-1} was reported for an amorphous WO_3 grown from WF_6 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.

WO_3 films have also been grown on a wide variety of substrates from WF_6 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 WO_3 films can be prepared from pyrolysis of WF_6 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 $W_{18}O_{49}$ and either tetragonal $WO_{2.9}$ or monoclinic $W_{20}O_{58}$.[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 WO_3 containing monoclinic WO_3.[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 WO_3 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 O_2 at 60 °C are in the range of 8–9 nm min^{-1}.[10]

TUNGSTEN ALKOXIDES

Tungsten alkoxides 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, $W(OC_2H_5)_n$ (n = 5, 6).[25] Pentakis(ethoxy)tungsten is a volatile liquid and hexakis(ethoxy)tungsten is a solid. Amorphous, adherent films of WO_3 (O:W ratio 2.7–3.2:1) were

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Table 2 Summary of electrochromic properties of CVD WO_3 films

Deposition method	Precursor	Structure	n[a] (cm^2C^{-1})	Response time Coloration	Response time Bleaching	Ref.
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
	$W(OEt)_x$	Amorphous	n.r.[c]	n.r.	n.r.	25
	$W(allyl)_4$	Crystalline	n.r.	n.r.	n.r.	31
PACVD	$W(CO)_6$	Amorphous	222	2 min	10 min	21–24
PECVD	WF_6	Amorphous	100	30 s		8,9

[a] In 1M $LiClO_4$ or $LiBF_4$ unless otherwise noted. [b] 1M H_2SO_4. 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.

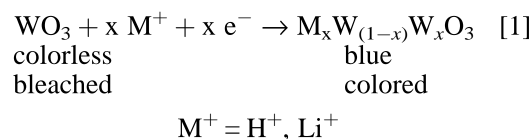
ORGANOMETALLIC TUNGSTEN COMPOUNDS

A number of organometallic tungsten compounds have been investigated as precursors for the CVD of tungsten metal,[6] including bis(cyclopentadienyl)-tungsten dihydride, $[(\eta^5\text{-Cp})_2WH_2]$[26] tris(methylvinylketone)tungsten, $[W(C_4H_6O)_3]$,[27] tris(butadiene)tungsten $[W(C_4H_8)_3]$[27] and tetra(allyl)tungsten, $[W(\eta_3\text{-}C_3H_5)_4$[28] Tungsten carbide films have been grown from $CpW(CO)_3H$, $Cp^*W(CO)_3H$, $(C_7H_8)W(CO)_3$, $(C_8H_{12}W(CO)_3$, toluene-$W(CO)_3$[29] and $Me_3C(CH_2)_2W{\equiv}CCMe_3$.[30] Deposition of tungsten oxide films from these precursors has not been reported.

Dark, reflective films (250 nm thick) deposited from $W(\eta^3\text{-}C_3H_5)_4$ 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 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 WO_3 films are summarized in Table 2. The color change is described by Eq. [1] and in Fig. 1:



$$WO_3 + x\,M^+ + x\,e^- \rightarrow M_xW_{(1-x)}W_xO_3 \quad [1]$$

colorless → blue; bleached → colored

$$M^+ = H^+,\ Li^+$$

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

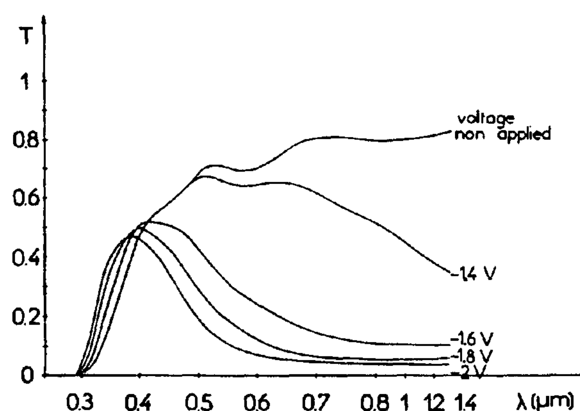


Figure 1 UV–Vis spectrum of WO_3 as a function of applied voltage.[13]

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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 WO_3 thin films prepared by PACVD from $W(CO)_6$ can have coloration efficiencies similar to those prepared by thermal CVD. Crystalline WO_3 films prepared by thermal CVD from $W(CO)_6$, however, have η values more than five times less than the amorphous films. Amorphous WO_3 films prepared by plasma-enhanced CVD using WF_6 had coloration efficiencies of 100 cm^2 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 organometallic precursors. Coloration efficiency is also dependent on the electrolyte, i.e. $LiClO_4$ or H_2SO_4.

RESPONSE TIME

The elapsed time for conversion of WO_3 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 WO_3 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 WO_3 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 WO_3 films with response times of $\approx$ 0.1 s have been reported.[33] WO_3 films sputtered from the metal oxide have response times measured in seconds, but recent results[34] show a strong dependence of the electrochromic properties on preparation methods. WO_3 films sputtered from the metal in an oxidizing atmosphere have longer response times, ranging from less than 30 s for colorizing 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 WO_3 has a density of 7.16 g cm^{-3}.

The coloration efficiencies for CVD WO_3 films are generally comparable and are sometimes better than films prepared by other deposition techniques. For example, amorphous WO_3 films prepared by thermal evaporation have η values ranging from 76 to 115 cm^2 C^{-1} compared with a value of 222 cm^2 C^{-1} for amorphous CVD films. Polycrystalline films grown by dc (direct current) or radiofrequency sputtering have η values ranging from 42 to 115 cm^2 C^1, compared to η values between 26 and 41 cm^2 C^{-1} for crystalline WO_3 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 WF_6 and $W(CO)_6$ indicate similar electrochromic behavior for films grown from either precursor (Table 2). The electrochromic properties, however,

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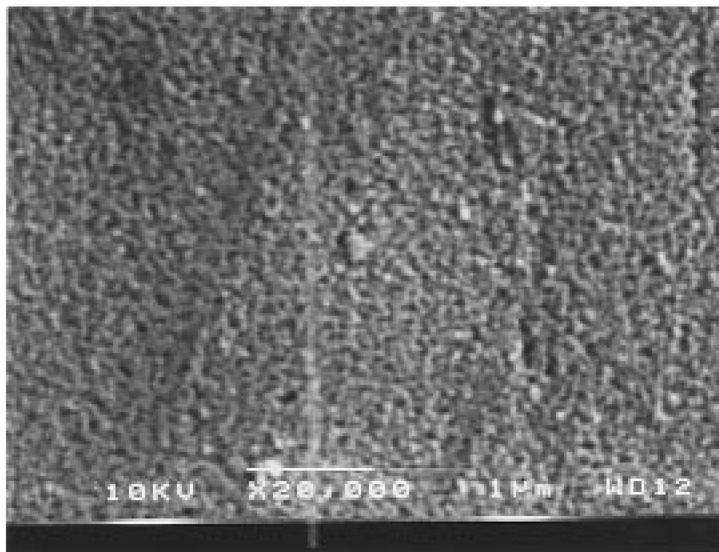

Figure 2 SEM of WO_3 film grown from $W(\eta^3\text{-}C_3H_5)_4$.

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 WF_6 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 WO_3 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 WO_3 which combine rapid growth with short response times at high color efficiencies appear to be warranted although widespread application of CVD WO_3 films in large-area devices such as window coatings may not be competitive with sol–gel or electrodeposition techniques.

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