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Thin Solid Films 392 (2001) 231–235

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Atmospheric pressure chemical vapor deposition of electrochromic tungsten oxide films

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Abstract

Tungsten oxide, WO_x, is a coloring layer commonly used in electrochromic windows and displays. Successful commercialization of these devices will require the deposition of WO_x layers with extremely uniform thickness and material properties over large areas at high speeds and low cost. We present a new atmospheric pressure chemical vapor deposition process that should be able to meet these goals. New liquid tungsten precursors have been found to have properties suitable for this application: sufficient volatility, reactivity to oxygen at substrate temperatures of 200–300°C, lack of reactivity to air and water at room temperature, and low viscosity (7 centiPoise at 40°C). The precursors are tungsten pentacarbonyl 1-methylbutylisonitrile and tungsten pentacarbonyl *n*-pentylisonitrile, $C_5H_{11}NCW(CO)_5$. These liquid precursors can be synthesized readily from commercially available reactants. Data on the composition and structure of the tungsten oxide films are presented, along with spectroscopic characterization of the films in transparent (oxidized) and colored (reduced) states. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemical vapor deposition; Tungsten; Oxides; Electrochromism

1. Introduction

Tungsten oxide is a key material in a wide variety of electrochromic devices, including 'smart' windows, displays and signs. By allowing the electrical control of light transmission and reflection, electrochromic windows can increase comfort, optimize illumination and reduce energy consumption in buildings. Electrochromic displays have good visibility in a variety of conditions and viewing angles, without constantly drawing power [1].

In its fully oxidized state, WO_3 is transparent throughout the visible and infrared regions of the spectrum. When it is reduced by injection of electrons along with neutralizing counter-ions, usually H^+ or Li^+, tungsten oxide absorbs and reflects light, taking on a blue–gray color in transmission.

Thin films of tungsten oxide have been made by a wide variety of methods. These include phyical methods, such as evaporation, sputtering and pulsed laser deposition, and chemical methods, such as chemical vapor deposition (CVD), sol–gel and electrochemical methods. CVD at atmospheric pressure (APCVD) has the advantages of scalability to large areas with uniform thickness and potentially low cost. For example, very large areas of energy-conserving fluorine-doped tin oxide coatings are made by APCVD on window glass over 3 m wide [2].

In this paper we investigate a new APCVD process for making tungsten oxide films using volatile liquid tungsten pentacarbonyl pentylisonitriles as precursors. These materials are air-stable liquids that we flash-vaporized and mixed with air, in order to deposit tungsten oxide on hot surfaces. We report the elec-

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PII: S0040-6090(01)01033-1

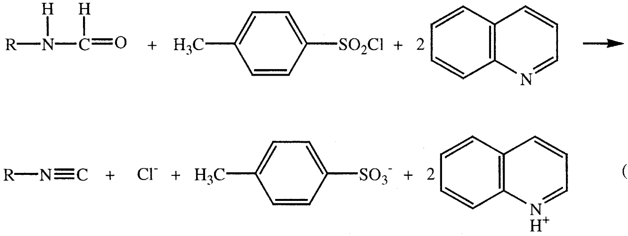
trochromic behavior of these films when they are reduced in the presence of protons or lithium ions.

2. Synthesis of volatile liquid tungsten compounds

The pentylisonitrile ligands were synthesized in two steps from commercially available pentylamines. First the amine is formylated by refluxing an equimolar mixture of the amine and ethyl formate [3]:

$$RNH_2 + HC(O)OC_2H_5 \rightarrow RNHC(O)H + C_2H_5OH \tag{1}$$

The resulting formamide is then dehydrated by reaction with *p*-toluenesulfonyl chloride and quinoline to form an alkyl isonitrile [4]:



(2)

The new tungsten compounds are readily synthesized by reacting the alkylisonitrile with tungsten hexacarbonyl with catalysis by palladium oxide in tetrahydrofuran at room temperature:

$$RNC + W(CO)_6 \rightarrow RNCW(CO)_5 + CO \tag{3}$$

Full details of this synthesis are given in Section 5.

3. Chemical vapor deposition experiments

Films of tungsten trioxide were deposited by CVD at atmospheric pressure. The reactant gas mixture was prepared by placing one of the liquid tungsten precursors, tungsten(0) pentacarbonyl 1-methylbutylisonitrile or tungsten(0) pentacarbonyl *n*-pentylisonitrile, in a syringe pump from which it was delivered at a steady rate between 1.5 and 14 ml/h into a Sonotek ultrasonic nozzle operated with 2.0–2.3 W of power at a frequency of 125 kHz. The resulting fog was entrained into an 8.0–9.0 l/min flow of nitrogen gas preheated to 180°C in order to vaporize the liquid droplets. This gas mixture was then mixed in a T joint with a flow of 1.0–1.5 l/min of oxygen gas before reaching the inlet to the reactor. The two precursors showed nearly identical reactivity, by comparison of samples 1–6 (Table 1).

The substrates used for electrochromism tests (samples 5 and 7) were commercial fluorine-doped tin oxide films on soda-lime glass [5] cut into 10 cm × 10 cm squares. All other films were deposited on bare 8 cm × 10 cm soda-lime glass. Atop all substrates were placed thin (300 μm) polished silicon pieces for Rutherford backscattering (RBS) and scanning electron microscopy (SEM) analysis. The substrates rested on a nickel plate that was electrically heated from below. The reactant gas mixture flowed over the substrate in a rectangular channel defined by another nickel plate held 1 cm above the substrate by thin nickel alloy (Hastelloy C) spacers that defined the sides of the gas flow channel. The substrates were held at temperatures between 275 and 350°C, while the top nickel plate was at 150°C. Films 32–125 nm thick grew at rates between 6 and 50 nm/min. The films were blue or brown in appearance after deposition.

Deposition rates of up to 50 nm/min were obtained by increasing precursor flow rates (samples 8–11). This was at the cost of reduced deposition efficiency, though, as thinner films resulted from a given precursor volume. As seen in Table 2, film density also decreased at high precursor flow rates, indicating more porous films.

The films were found to contain tungsten and oxygen in nearly stoichiometric ratio WO_3 by RBS experiments on samples deposited on silicon. No carbon or

Table 1
Deposition conditions for some WO_x films

Sample no.	Precursor	Substrate temp. °C	N_2 flow rate l/min	O_2 flow rate l/min	Volume of W precursor ml	W precursor flow rate ml/h	Deposition rate nm/min
1	*n*-Pentyl	275	9.0	1.0	0.2	1.5	9.6
2	*n*-Pentyl	300	9.0	1.0	0.2	1.5	14.
3	*n*-Pentyl	350	9.0	1.0	0.2	1.5	9.4
4	1-MeBu	275	9.0	1.0	0.2	1.5	8.8
5	1-MeBu	300	9.0	1.0	0.2	1.5	16.
6	1-MeBu	350	9.0	1.0	0.2	1.5	9.6
7	*n*-Pentyl	300	9.0	1.0	n/a	1.5	n/a
8	*n*-Pentyl	300	8.0	1.5	0.15	1.5	7.2
9	*n*-Pentyl	300	8.0	1.5	0.15	3.0	15
10	*n*-Pentyl	300	8.0	1.5	0.15	9.0	34
11	*n*-Pentyl	300	8.0	1.5	0.15	14.	50.

Table 2
Thicknesses, composition and densities of some WO_x films

Sample no.	Color	Formula	Thickness nm	W area density cm^{-2}	Density $g\ cm^{-3}$
1	Blue	$WO_{3.1}$	77	9.1×10^{16}	4.6
2	Blue	$WO_{3.1}$	115	1.6×10^{17}	5.4
3	Blue	$WO_{3.4}$	75	8.8×10^{16}	4.6
4	Blue	$WO_{3.0}$	70	9.4×10^{16}	5.2
5	Blue	$WO_{3.2}$	125	1.8×10^{17}	5.6
6	Blue	$WO_{3.2}$	77	1.1×10^{17}	5.6
7	Brown	$WO_{3.3}$	110	1.7×10^{17}	6.2
8	Brown	$WO_{3.5}$	43	4.9×10^{16}	4.5
9	Brown	$WO_{3.2}$	45	4.0×10^{16}	3.5
10	Brown	$WO_{2.8}$	34	3.3×10^{16}	3.7
11	Brown	$WO_{2.9}$	32	2.8×10^{16}	3.3

nitrogen could be detected (<10 at.%). The formulas of the films were determined by integration of the RBS data, and SEM was used to determine the thickness of the films. Combination of the RBS data and thicknesses yielded the densities shown. The films are thinner than ideal for most electrochromic devices simply for ease of RBS analysis. No problems are foreseen in the deposition of thicker WO_3 films with these precursors.

4. Electrochromic measurements

Electrodes were attached to the fluorine-doped tin oxide with indium solder and the films were immersed in one of two electrolytes: lithium perchlorate (1 M) solution in 95:5 w/w propylene carbonate/water, or sulfuric acid solution (1 M) in water. Reduction of the films was accomplished by making the tin oxide/tungsten oxide films the cathodes in these electrolytes, with inert anodes. Voltages from -3.1 to $+4.8$ V were applied, with positive voltages generating or deepening a blue color and negative voltages causing bleaching. The films were stable except at the highest voltage, $+4.8$ V, when the lithium perchlorate electrolyte tended to dissolve the films. Transmission spectra for the films were recorded on a Hitachi U-4001 spectrophotometer after various reduction and oxidation times. These data are presented in Figs. 1 and 2.

These spectra show the expected coloration of the films after reduction. The re-oxidation (bleaching) of the films is considerably slower than their coloration when $LiClO_4$ is used as the electrolyte. This tendency has been observed for other tungsten oxide films [6]. For sulfuric acid electrolyte, coloring and bleaching times were both a few minutes at maximum. The less dense films respond more quickly and to a greater degree, indicating faster and more extensive diffusion of the ions into the more open structure of these films.

5. Experimental details of the chemical synthesis

5.1. Synthesis of 1-methylbutylformamide, $CH_3CH_2CH_2CH(CH_3)NHC(=O)H$

1-Methylbutylamine (2-pentylamine, available from Lancaster Synthesis) (48.7 g, 0.55 mol) and ethyl formate (43.5 g, 0.58 mol) were added to a Schlenk flask, degassed, and refluxed at 85°C for 12 h. The excess ethyl formate and ethanol by-product were removed by vacuum distillation to yield crude, colorless 1-methylbutylformamide (53.0 g, 82%), which was used without

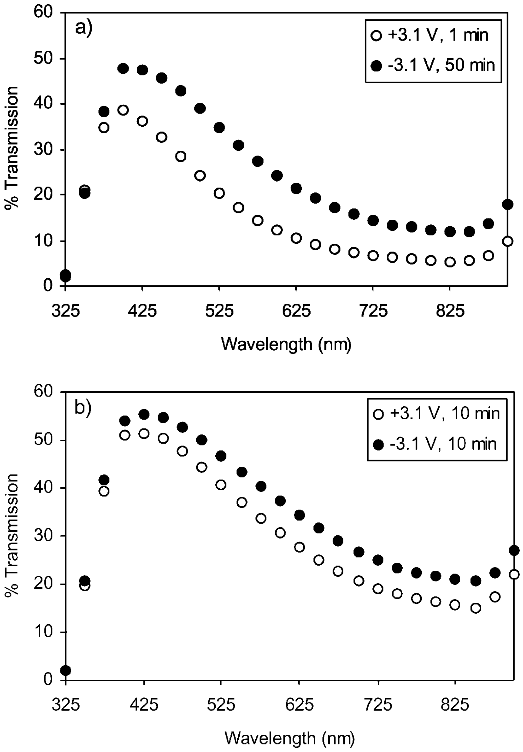


Fig. 1. Transmission spectra of sample 5 after reduction (open circles) and oxidation (closed circles) (a) in lithium electrolyte and (b) in acid electrolyte.

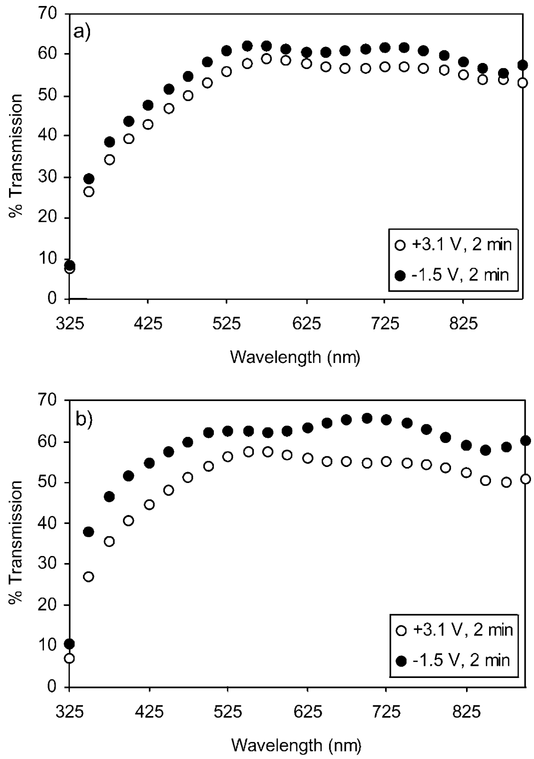


Fig. 2. Transmission spectra of sample 7 after reduction (open circles) and oxidation (closed circles) (a) in lithium electrolyte and (b) in acid electrolyte.

further purification. IR (cm^{-1}): 1656, strong, NC(=O). ^{1}H-NMR (C_6D_6):

(δ7.76 ppm, singlet,
1H, $CH_3CH_2CH_2CH(CH_3)NHC(O)\mathbf{H}$);

(δ3.99 ppm, septet,
1H, $CH_3CH_2CH_2C\mathbf{H} \times (CH_3)NHC(O)H$);

(δ1.04 ppm, multiplet,
2H, $CH_3CH_2C\mathbf{H}_2CH(CH_3)NHC(O)H$);

(δ0.98 ppm, multiplet,
2H, $CH_3C\mathbf{H}_2CH_2CH(CH_3)NHC(O)H$);

(δ0.77 ppm, multiplet,
6H, $C\mathbf{H}_3CH_2CH_2CH(CH_3)NHC(O)H$);

5.2. Synthesis of 1-methylbutylisonitrile, $CH_3CH_2CH_2CH(CH_3)NC$

A dark brown solution of *p*-toluenesulfonylchloride (58.6 g, 0.31 mol) dissolved in quinoline (132.3 g, 1.02 mol) was heated to 85°C in a three-neck round bottom flask equipped with a distillation head to a condenser and Schlenk flask, and an addition funnel with 1-methylbutylformamide (31.0 g, 0.26 mol). The system was evacuated (80 mtorr) and the 1-methylbutylformamide was added over 20 min. A clear, colorless liquid distilled from the reaction and was collected in the Schlenk flask chilled in liquid nitrogen. The volatiles were collected for 20 min after addition completed and the crude product contained large quantities of quinoline. The crude product was distilled under low pressure (59–62°C at 19 torr) using a vigreux column producing clear, colorless 1-methylbutylisonitrile (23.0 g, 81%). IR (cm^{-1}): 2138, vs., $R\mathbf{N}\equiv\mathbf{C}$. ^{1}H-NMR ($C_6D_6$):

(δ2.85 ppm, septet,
1H, $CH_3CH_2CH_2C\mathbf{H}(CH_3)NC$);

(δ1.18 ppm, multiplet,
1H, $CH_3CH_2C\mathbf{H}_2CH(CH_3)NC$);

(δ1.04 ppm, multiplet,
2H, $CH_3C\mathbf{H}_2CH_2CH(CH_3)NC$);

(δ0.80 ppm, multiplet,
1H, $CH_3CH_2CH_2CH(C\mathbf{H}_3)NC$);

(δ0.74 ppm, multiplet,
3H, $CH_3CH_2CH_2CH(C\mathbf{H}_3)NC$);

(δ0.61 ppm, multiplet,
3H, $C\mathbf{H}_3CH_2CH_2CH(CH_3)NC$);

5.3. Synthesis of tungsten(0) pentacarbonyl 1-methylbutylisonitrile, $(CH_3CH_2CH_2CH(CH_3)NC)W(CO)_5$

Tungsten hexacarbonyl (10.0 g, 0.028 mol) and palladium (II) oxide (0.02 g, 0.00016 mol) were charged in a 250-ml Schlenk flask and the flask was evacuated and backfilled with dry nitrogen gas three times. Dry tetrahydrofuran (150 ml) was added by cannula and the mixture was slightly heated to facilitate the dissolution of the tungsten hexacarbonyl. To this, 1-methylbutylisonitrile (3.00 g, 0.031 mol) was added drop-wise over 10 min. The solution effervesced vigorously (evolution of carbon monoxide) and was allowed to stir for 15 min after addition was complete. The yellow solution was filtered through celite to remove the palladium oxide, and volatiles were removed in vacuo. A low viscosity orange liquid (11.2 g) resulted. Purification by falling molecular film distillation at 65°C and $< 3 \times 10^{-3}$ torr gave yellow tungsten pentacarbonyl 1-methylbutylisonitrile (8.9 g, 75% yield). Melting point: 9°C. ^{1}H-NMR δ: 2.78 (m, 1H), 1.1–0.82 (overlapping m, 4H), 0.58 (t, 3H), 0.53 (d, 3H). Viscosity (at 40°C): 7.03 centiPoise. Molecular complexity: 1.1 (by melting point of *p*-xylene solution). Calculated: C, 31.38; H, 2.63; N, 3.33. Found: C, 31.38; H, 2.42; N, 3.26.

Tungsten pentacarbonyl *n*-pentylisonitrile was prepared by the same procedure as tungsten pentacarbonyl 1-methylbutylisonitrile, except that *n*-pentylamine was used in place of 1-methylbutylamine.

These precursors are stable in contact with air and water at room temperature. Visible light causes decomposition (discoloration to green, brown and eventually formation of a black precipitate).

6. Conclusions

Tungsten oxide films were deposited at atmospheric pressure from the vapors of convenient, air-stable precursors, tungsten pentacarbonyl pentylisonitriles. This method is rapid and readily scalable to large areas. The films show electrochromic behavior with either protons or lithium counter-ions. The deposition conditions affect the density of the films, with less dense films showing more rapid and more extensive coloration and bleaching. Further optimization of the film thickness and deposition conditions is needed to produce electrochromic effects with a higher contrast ratio.

Acknowledgements

This work was supported in part by the US Department of Energy through a subcontract from the National Renewable Energy Laboratory, and the US National Science Foundation.

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