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Atmospheric Pressure Chemical Vapor Deposition of Crystalline Monoclinic WO_3 and WO_{3-x} Thin Films from Reaction of WCl_6 with O-Containing Solvents and Their Photochromic and Electrochromic Properties

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The atmospheric pressure chemical vapor deposition (CVD) reaction of WCl_6 with a variety of reactants (ethanoic anhydride, ethanoic acid, ethyl ethanoate, methanol, ethanol, 2-propanol, 2-methyl-2-propanol, and water) was examined on glass substrates. The deposited films displayed strikingly different morphologies with differing reactants under otherwise identical conditions. Full characterization revealed that the films were all monoclinic WO_3, but the different morphologies lead to significant differences in the functional properties of the deposited films, such as photochromism and photocatalysis. The effects of the CVD parameters on deposited films were extensively studied for the reaction of WCl_6 with ethanoic anhydride.

Introduction

Tungsten oxide (WO_3) has been the subject of extensive investigation since the demonstration of the photochromic and electrochromic properties of amorphous thin films by Deb.[1] Thin films of tungsten oxide can be utilized in different devices such as "smart windows", anti-dazzle mirrors, and information displays.[2] While the electrochromic properties of WO_3 have been well investigated,[3,4] our group is more interested in the photochemistry of tungsten oxide, in particular related to architectural glass applications, which are less investigated.[5] The first report of photochromism in polycrystalline WO_3 thin films is by Gavrilyuk et al.[6] who deposited thin films by thermal deposition in vacuo, while most recently Bulhões investigated crystalline thin films of WO_3 and WO_3:X (where X = Ti, Nb, Ta, and Zr) deposited via dip coating.[7] Georg has published work on the gasochromic coloration of WO_3 films[8] for use in architectural glass but uses a DC magnetron sputtering method to deposit the WO_3 films, although this relies on the use of complicated ancillary equipment for the film bleaching and coloration. One of the requirements for large area coating of architectural glass is the integration of the coating technology with float glass production techniques for high-volume low-cost coating to ensure the coating process is economically viable. This generally entails in-line processing at atmospheric pressure, a process for which atmospheric pressure chemical vapor deposition (APCVD) is ideally suited[9,10] Researchers have tried depositing films for electrochromic studies via a variety of methods including thermal evaporation,[1] sol−gel,[11] spray pyrolysis,[12] and pulsed laser deposition.[13] CVD methods to tungsten oxide were reviewed by Kirss and Meda and include the use of WF_6, $W(CO)_6$, $W(OC_2H_5)_n$ (where $n = 5$ or 6), and organometallic tungsten compounds.[14] All these methods have drawbacks, from the use of the fluorinated precursor WF_6, the difficulty of synthesising $W(OC_2H_5)_n$ in high yields,[15,16] to the two-step process of deposition followed by oxidation required for the organometallic precursors. Recently a one-step APCVD route to WO_3 from tungsten pentacarbonyl alkylisonitrile precursors was demonstrated, which while having the advantage of being air stable does require the synthesis of a light-sensitive precursor.[17] A recent APCVD method for the deposition of WO_3 from reaction of $WOCl_4$ and ethanoic anhydride or ethanol which despite producing extremely high quality films rely on the use of $WOCl_4$, which has a narrow window in which it generates sufficient vapor pressure without decomposing.[18] A low-cost

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Table 1. APCVD Experimental Conditions for the Reaction of WCl_6 + Reactant

reactant	WCl_6 molar flow rate (mol/min)	reactant molar flow rate (mol/min)	gas-phase molar ratio (WCl_6/reactant)	plain flow (L/min)	set temp (°C)	WDX results (at. %)					growth rate (nm/min)	XRD	Raman	film color
						W	O	Cl	C	Si				
ethanoic anhydride	0.0075	0.2	1:25	10	625	22.8	75.0	0	2.1	0.1	1000	m-WO_3	m-WO_3	yellow
ethanol	0.0075	0.075	1:10	10	625	23.4	71.6	0.4	3.7	0.8	800	m-WO_3 (020)	WO_3-like	blue
methanol	0.0075	0.075	1:10	10	625	28.8	44.1	0.1	6.2	20.8	300	m-WO_3	WO_3-like	blue
ethanoic acid	0.0075	0.03	1:4	10	625	4.7	68.6	0.1	2.4	24.2	200	m-WO_3	m-WO_3	gold
water	0.0075	0.375	1:50	10	625	3.8	67.2	0	2.3	26.7	225	m-WO_3	m-WO_3	yellow
ethylethanoate	0.0075	0.15	1:20	10	625	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*
2-propanol	0.0075	0.075	1:10	10	625	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*
2-methyl-2-propanol	0.0075	0.075	1:10	10	625	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*

[a] No film was deposited.

route to tungsten oxide coatings from readily available, inexpensive laboratory reagents is needed. After the use of solid $MoCl_5$[19] with an organophosphine for the deposition of molybdenum phosphide was demonstrated, it was envisaged that the use of WCl_6 for the deposition of WO_3 should be possible.

Here we report the deposition of WO_3 films from reaction of WCl_6 and a wide variety of co-reactants. Interestingly, the morphology and functional properties, such as photochromism and photocatalysis, are dependent on the specific co-reactant used.

Experimental Section

APCVD experiments were conducted using SiCO-coated (SiCO is a barrier layer to stop diffusion of ions from the glass into the CVD produced film) float-glass substrates (90 mm × 45 mm × 4 mm) in a horizontal-bed cold-wall APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (30−40 °C), propan-2-ol, and subsequent air drying. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt−Rh thermocouple. Measurements indicated temperature gradients of less than 25 °C at 500 °C across the glass substrates. All gas-handling lines, regulators, and flow valves were made of stainless steel and were $^1/_4$ in. internal diameter, except for the inlet to the mixing chamber and the exhaust line from the apparatus that were $^1/_2$ in. internal diameter. Nitrogen (99.99%), obtained from British Oxygen Company and used directly from the cylinder, was preheated by passing along lengths of stainless steel tubing inserted inside a furnace. Pt−Rh thermocouples and Eurotherm heat controllers monitored the temperatures of all gas inlet lines. Tungsten hexachloride (99.9%-W) was purchased from Strem Chemicals, Inc., ethanoic anhydride (98%), ethanoic acid (99.8%), ethyl ethanoate (99.5+%), methanol (99+%), ethanol (denatured), 2-propanol (99+%), and 2-methyl-2-propanol (99+%) were all purchased from Aldrich. Water was double distilled “in house”. WCl_6 and one of the reactant chemicals were placed into separate heated stainless steel bubblers, and the vapors generated introduced into the gas streams by passing hot nitrogen gas through the bubblers. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with nitrogen at 150 °C for 60 min before deposition. Deposition experiments were conducted by heating the horizontal bed reactor and the bubblers to the required temperatures before diverting the nitrogen line through the bubblers and hence to the reactor. At the end of the deposition, the bubbler lines were closed and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to ca. 150 °C before it was removed. Coated substrates were handled and stored in air. The large coated glass samples were broken up for subsequent analysis by X-ray photoelectron spectroscopy (XPS), wavelength dispersive analysis of X-rays (WDX), scanning electron microscopy (SEM), Raman spectroscopy, sheet resistance, glancing angle X-ray diffraction (XRD), and Scotch tape tests.

X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated Cu Kα_1 radiation ($\lambda_1 = 1.5406$ Å) utilizing a position sensitive detector. The diffractometer was used in low-incident geometry (5°). To confirm suspected preferred orientation, the diffractor was used in $\theta-2\theta$ geometry. Data manipulation was performed using Bruker EVA software, and samples were indexed using a unit cell and compared to database standards. WDX was obtained on a Phillips XL30 ESEM (accelerating voltage 10 kV) using Oxford Instruments instrument control and Inca Wave analytical software. SEM was obtained on a JEOL 6301F (accelerating voltage of 20 kV) using Oxford Instruments ISIS software. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium−neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. X-ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focused (300-μm spot) monochromatic Al Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging, and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Depth profile measurements were obtained using argon beam sputtering (etch voltage 5 kV). Electrical conductivity was determined by a 4-probe measurement on glass substrates.

Deposition conditions are shown in Tables 1 and 2. Metal precursor:reactant gas-phase molar ratios were calculated using vapor pressure data[20,21] and nitrogen flow rates. In all cases, the deposition run time was 1 min. The film thickness measurements were determined using SEM of a cross section of the film/substrate taken from an identical point on each substrate (midpoint of substrate, 4 cm from leading edge). WDX was used to analyze all films that were deposited. The silicon atomic percentages are shown because in cases where breakthrough to the underlying glass substrate was observed accurate quantification of oxygen in the film is impossible.

Results

Effect of Changing Reactant. The APCVD reaction of WCl_6 with a variety of reactants was examined, with the

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Table 2. APCVD Experimental Conditions for the Reaction of WCl_6 + Ethanoic Anhydride

WCl_6 molar flow rate (mol/min)	reactant molar flow rate (mol/min)	molar ratio (WCl_6/reactant)	plain flow (L/min)	set temp (°C)	WDX results (at. %) W	O	Cl	C	Si	growth rate (nm/min)	XRD	Raman
0.0075	0.0075	1:25	0.2	625	22.8	75.0	0	2.1	0.1	1000	m-WO_3	m-WO_3
0.0075	0.0075	1:25	0.2	450	23.9	66.3	0.1	0.9	8.8	200	m-WO_3	m-WO_3
0.004	0.1	1:25	20	500	*a*	*a*	*a*	*a*	*a*	*a*	m-WO_3	m-WO_3
0.004	0.1	1:25	10	500	28.1	65.4	0.1	6.5	0	725	m-WO_3	m-WO_3
0.004	0.1	1:25	5	500	33.8	30.6	26.1	4.9	4.6	n/d[b]	m-WO_3	m-WO_3
0.004	0.1	1:25	2	500	10.6	71.9	0.8	2.0	14.6	n/d	m-WO_3	m-WO_3
0.003	0.1	1:30	10	500	37.9	59.4	0.4	2.2	0.1	475	m-WO_3	m-WO_3
0.01	0.1	1:10	10	500	6.0	62.9	0.1	1.6	29.3	n/d	m-WO_3	m-WO_3
0.00075	0.1	1:125	10	500	1.3	68.3	0.1	1.1	29.3	n/d	m-WO_3	m-WO_3

[a] No film was deposited. [b] Not determined.

optimized deposition conditions shown in Table 1. It was found that the use of ethanoic anhydride, ethanol, methanol, ethanoic acid, and water all caused the deposition of blue or yellow films. Complete substrate coverage was obtained using ethanol or ethanoic anhydride as the reactant, with less coverage observed for methanol, ethanoic acid, and water, the films having full-width coverage but being localized to the central third of the substrate. All films were adherent to the substrate and passed the “Scotch tape test”. The use of ethyl ethanoate, 2-propanol, and 2-methyl-2-propanol did not afford films under any conditions. Deposition temperature could not be increased above 650 °C due to the melting point of the glass substrates but decreased substrate temperature, variation of total N_2 flow rate (plain flow), and variation of reactant molar ratios were examined. The failure of ethyl ethanoate to deposit films of sufficient quality was unexpected, as previously this has been found to be a superior reactant for the deposition of high-quality WO_3 films during reaction with $WOCl_4$.[18] Of the films deposited, the use of water or ethanoic acid as the reactant afforded transparent pale golden colored films, whereas ethanoic anhydride deposited almost opaque yellow films. Deposition using ethanol and methanol both gave blue films, deep-blue opaque films from ethanol and pale-blue, partially transparent films from methanol.

Chemical and Structural Analysis. WDX was used to analyze the films deposited at a substrate temperature of 625 °C. At an accelerating voltage of 10 kV, only the films deposited from ethanoic anhydride and ethanol were sufficiently thick that no appreciable breakthrough to the underlying substrate was observed. In these cases, a metal:oxygen ratio could be determined. For the yellow films deposited using ethanoic anhydride, the results indicate overstoichiometric tungsten oxide, $WO_{3.3(+/-0.05)}$, whereas the blue films deposited using ethanol surprisingly had a $WO_{3.0(+/-0.03)}$ stoichiometry (a blue coloration in WO_3 is typical of the reduced form of tungsten oxide, WO_{3-x}). The overstoichiometry of oxygen is attributed to water within the films,[22] and indeed water was detectable in both of these films using Fourier-transform (FT) IR spectroscopy. In all cases, it should be noted that chlorine contamination was negligible and that carbon contamination was low. The absence of chlorine contamination in the films deposited using ethanoic anhydride was initially thought surprising because this reactant has no acidic protons to provide the most obvious leaving group for chlorine, HCl. However the ethanoyl groups could eliminate chloride in the form of volatile ethanoyl chloride.

Film thickness was measured using cross-sectional SEM. The deposition time in each case was 1 min, and the number of moles of WCl_6 was identical. The results are an average of all depositions performed under the specified conditions and show that the films deposited from ethanoic anhydride (1000 nm) and ethanol (800 nm) were much thicker than those deposited from methanol (300 nm), ethanoic acid (200 nm), or water (225 nm). The film densities were not measured, and although the change in film thickness may relate to a change in film porosity, as opposed to a change in the amount of tungsten species deposited, SEM imaging (Figures 1, 3, and 4) indicated that films deposited using ethanoic anhydride had the lowest porosity and those deposited using methanol a much higher porosity. This indicates that under similar reactant flow rates greater amounts of tungsten species were deposited using ethanoic anhydride than using methanol. SEM was also used to examine the film microstructures. It was observed that changing the reactant dramatically changed the surface microstructure of the film. The films deposited from ethanoic anhydride (Figure 1) showed an agglomeration of submicrometer cubelike crystallites, whereas films deposited from ethanol (Figure 2) appeared as a “mat” of discrete needles orientated parallel to the substrate. The films deposited using methanol (Figure 3) as the reactant had a

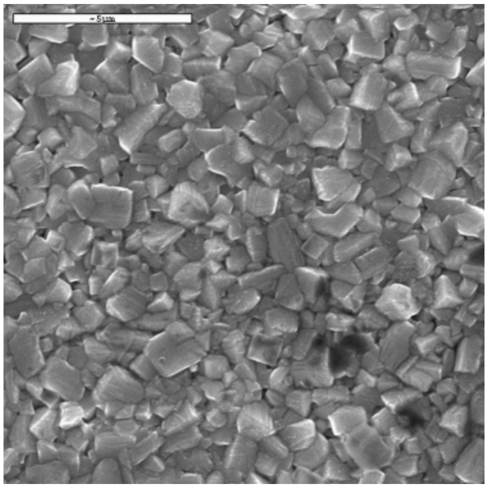

Figure 1. SEM of film deposited from WCl_6 and ethanoic anhydride at 625 °C.

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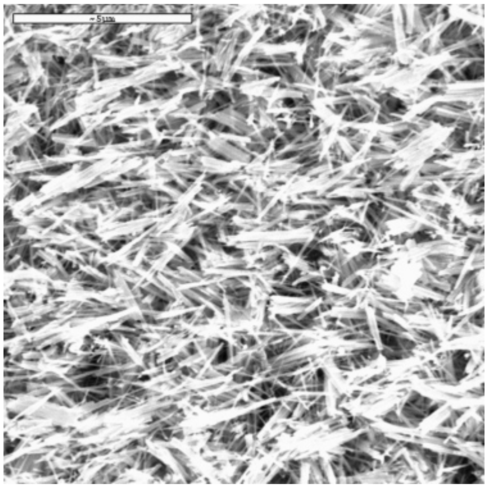

Figure 2. SEM of film deposited from WCl_6 and ethanol at 625 °C.

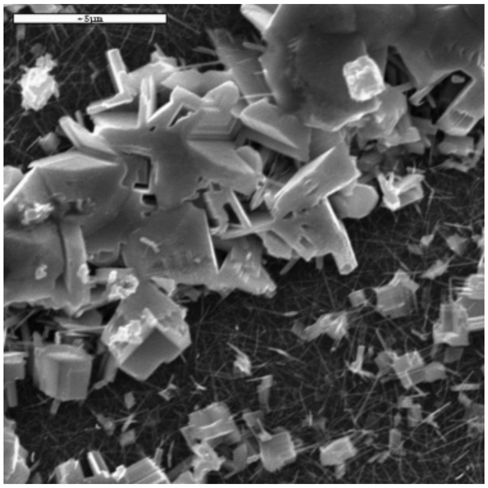

Figure 3. SEM of film deposited from WCl_6 and methanol at 625 °C.

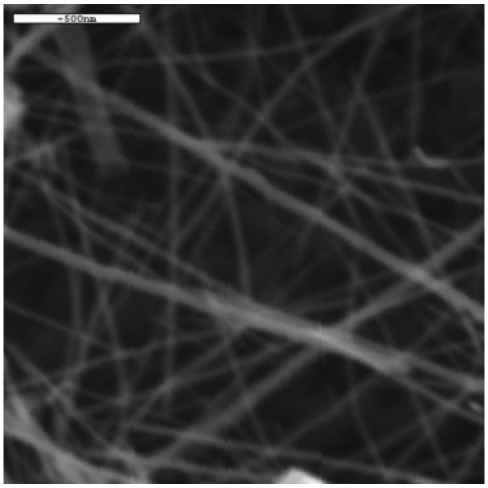

Figure 4. Close-up SEM of film deposited from WCl_6 and methanol at 625 °C.

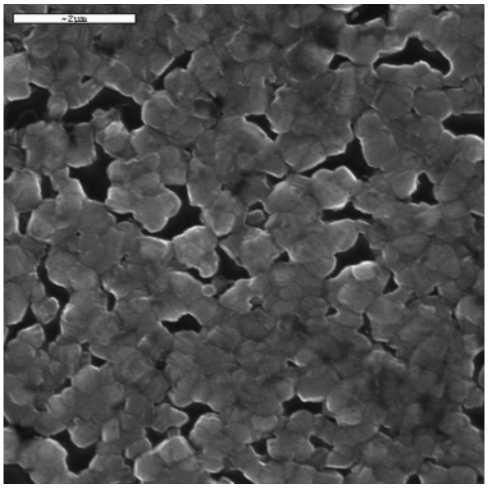

Figure 5. SEM of film deposited from WCl_6 and ethanoic acid at 625 °C.

Figure 6. SEM of film deposited from WCl_6 and water at 625 °C.

structure somewhere between that of ethanoic anhydride and that of ethanol, with large cubic crystallites growing out of the surface in long chains with an extended structure of interconnecting "wires" parallel to the substrate (Figure 4). Films deposited using ethanoic acid (Figure 5) have a similar surface to films deposited using ethanoic anhydride, although the crystallites appear smaller and less cubic, and there are what appears to be large voids between the crystallites. To further highlight the differences in surface morphologies obtained with changes in reactant the films deposited from WCl_6 and water (Figure 6) have the appearance of hexagonal plates, many of which are orientated perpendicular to the substrate surface. In general, other than the films deposited using ethanoic acid, these morphologies are unlike those seen in the literature for films deposited from tungsten hexaphenoxide via aerosol-assisted (AA)CVD on glass substrates,[23] from tungsten(VI) ethoxide via sol–gel on silicon substrates,[11] or from tungsten hexacarbonyl via LPCVD on silicon.[24] The films deposited using ethanoic acid have some similarities with the crystallites formed from the annealing of black tungsten deposited onto silicon via the decomposition of tungsten hexacarbonyl at low pressure.[25]

The films deposited at 625 °C were analyzed using glancing-angle XRD. For the films deposited using ethanoic anhydride (a = 7.341(7), b = 7.557(6), c = 3.860(4) Å), water (a = 7.39(2), b = 7.49(2), c = 3.87(1) Å), and ethanoic acid (a = 7.33(1), b = 7.539(9), c = 3.857(6) Å), the diffraction pattern matched that of monoclinic WO_3 (a =

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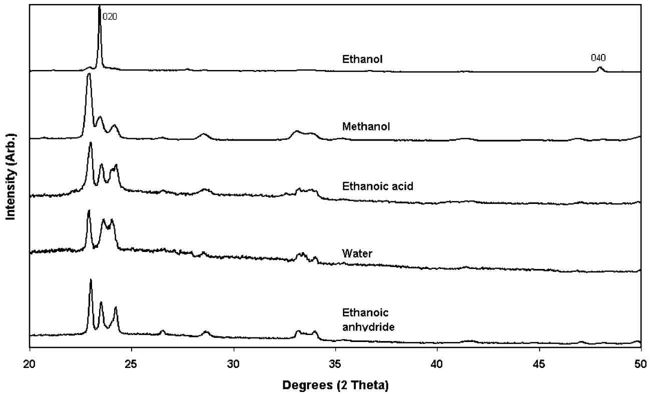

Figure 7. XRD patterns for films deposited from WCl_6 and various reactants at 625 °C.

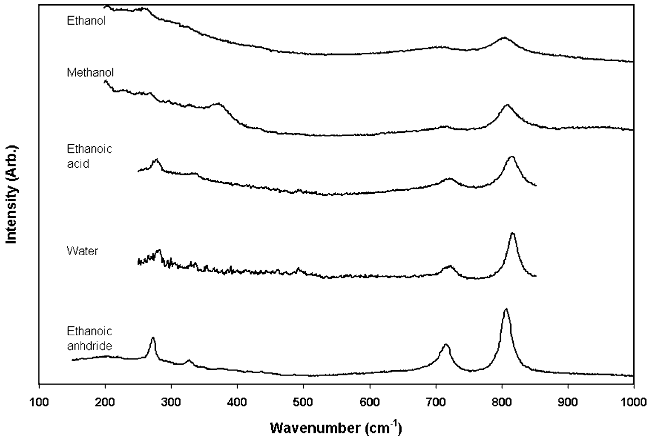

Figure 8. Raman spectra for films deposited from WCl_6 and various reactants at 625 °C.

7.285, $b = 7.517$, $c = 3.835$ Å).[26] Also the pale-blue films deposited using methanol ($a = 7.353(9)$, $b = 7.564(7)$, $c = 3.868(5)$ Å) gave a pattern matching that of monoclinic WO_3. The films deposited from ethanol ($a = 7.36(9)$, $b = 7.42(9)$, $c = 3.87(9)$ Å) showed striking preferred orientation with the $\langle 020 \rangle$ and $\langle 040 \rangle$ diffraction peaks greatly enhanced (Figure 7).

Further analysis was performed with Raman spectroscopy (Figure 8). The films deposited from the reaction of WCl_6 and ethanoic anhydride were clearly identifiable as crystalline monoclinic WO_3,[27,28] with strong bands at 808, 717, 329, and 274 cm^{-1}, as were the films deposited using water and ethanoic acid. The films deposited using methanol had the same principal bands at 811 and 716 cm^{-1} but had a more amorphous appearance overall, with broader less well defined peaks and a general increase in intensity at lower wavenumbers with a significantly different spectrum in the region of 200−400 cm^{-1}. This region has been identified as containing $W^{4+}-O$ and $W^{5+}-O$ vibrations in amorphous WO_{3-x} tungsten oxides[29] and may suggest the presence of reduced species in this film, which is also indicated by the pale-blue coloration of films deposited using methanol. The films deposited using ethanol are different again, although they have more in common with films deposited using methanol than those deposited from ethanoic anhydride.

XPS was used to analyze the surface of the as-deposited films. The films were exposed to air after deposition and prior to XPS analysis, although the period of time was minimized to try and reduce the effect of atmospheric oxidation. A sample film deposited from reaction of WCl_6 and ethanoic anhydride showed a surface tungsten ionization $W4f_{7/2}$ at 35.6 eV, corresponding to fully oxidized (W^{6+}) WO_3.[30] The only other peak was the companion $W4f_{5/2}$ peak with no evidence for any other tungsten species. The peak area ratio (0.75) and the splitting (2.2 eV) between the $4f7_{7/2}$ and the $4f7_{5/2}$ were in agreement with theory, confirming that no other tungsten environments were present.[3] Etching showed that carbon contamination was entirely surface limited and that chlorine contamination was also below detection limits. Similarly the sample films deposited using acetic acid ($W4f_{7/2}$ 35.5 eV) or water ($W4f_{7/2}$ 35.6 eV) as the reactant had only one tungsten environment, no chlorine contamination, and carbon contamination in the bulk of 5 and 3 at. %, respectively. The representative film deposited using methanol as a reactant had a doublet in the W region, but the peaks were broadened and slightly asymmetric. Peak fitting using full-width half-maximum (fwhm) and peak area ratio constraints indicated 2 sets of $W4f_{7/2}$ peaks. The dominant peak was at 35.5 eV (W^{6+}) with a much smaller peak observed at 34.3 eV (W^{5+}).[30] The ratio of the peak areas was ~85% W^{6+} to 15% W^{5+}. The presence of a W^{5+} environment supports the observation that the film was pale blue in color. The film deposited from WCl_6 and ethanol had a very poor peak shape in the W4f region, being very broad and asymmetric. Deconvolution of the peak, again using fwhm and peak area constraint, revealed 3 $W4f_{7/2}$ peaks. The peak fitting did not precisely model the experimental data, with slight deviation at the high-energy side, but it was clear that there was a W^{6+} environment (35.5 eV), a W^{5+} environment (34.4 eV), and a W^{4+} (33.3 eV) environment in an approximate ratio of 3:2:1.[30] The presence of such a large relative amount of reduced tungsten species would explain the very deep blue color observed in this film. No chlorine contamination was detected in either of the alcohol-deposited films, but carbon contamination was higher near the surface (~15−20%) than seen for the other films. An exact determination was not made because the bulk of the films were not examined. However, it was shown that the carbon was graphitic rather than carbide and was reduced even after short etch periods (~10%), indicating that the film bulk probably had low levels of carbon contamination, similar to that seen in the other films. Additionally the WDX results (Table 1) for films deposited using ethanol as the reactant showed similar levels of carbon contamination (3.7%) to those deposited using ethanoic anhydride (2.4%)

Films deposited using WCl_6 as the metal source and ethanoic anhydride, ethanoic acid, or water as the reactant are fully oxidized monoclinic WO_3. The films deposited using the alcohols methanol and ethanol were reduced tungsten oxide; deposition using methanol yielded a partially

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reduced film ($WO_{2.93}$ from XPS data) with an XRD pattern matching monoclinic WO_3 whereas deposition using ethanol gave a heavily reduced film ($WO_{2.65}$ from XPS data), which while appearing to be monoclinic WO_3 exhibited strong preferred orientation in the ⟨020⟩ plane. No films were deposited using 2-propanol or 2-methyl-2-propanol. It is postulated that the reduction observed in the films deposited using methanol and ethanol may be related to the lower oxygen balance in these precursors, relative to ethanoic anhydride and ethanoic acid. The lack of film deposition from 2-propanol or 2-methyl-2-propanol may be related to the shielding of the oxygen in these molecules, making approach of the WCl_6 less favorable. Despite all the films appearing as monoclinic WO_3 using XRD and Raman they had extremely varied morphologies ranging from needles (ethanol) through plates (water) to cubic crystallites (ethanoic anhydride, ethanoic acid). Deposition using methanol exhibited an intermediate morphology of needles and cubic crystallites. It is possible that some of the morphological differences result from gas-phase precipitation, especially for the films deposited using ethanol in which some of the needles observed appear unconnected to the substrate. It is surprising that given the depositions took place on identical substrates at the same temperature that such different morphologies were obtained. It is apparent that the morphology is intricately with the reaction chemistry taking place, either in the gas phase or at the surface. It is possible that the greater amount of carbon detected at the surface of the alcohol deposited films, if it extends into the bulk, could be responsible for the morphological differences.

Physical Properties. The transmission and reflection properties of the as-deposited films were examined in the visible near-IR region. It was shown that films deposited using ethanol were almost totally opaque, films deposited using ethanoic anhydride or methanol had a peak transmission of between 10 and 15%, films deposited using ethanoic acid had a peak transmission of ∼30%, but the films deposited using water were much more transparent yielding a figure of ∼70% transmission. None of the films had a significant reflection component (<10%). The optical band gap of the transparent film deposited from the reaction of WCl_6 and water was determined by plotting $(\alpha h\nu)^{1/2}$ against $h\nu$ (Tauc plot).[31] It should be noted that the experimental band gaps measured from the Tauc plot only give an indication of the band gap as they apply to *k*-nonconservation studies. However the values measured at 2.5 eV are similar to the literature value given by Salje for crystalline WO_3 of 2.58 eV.[32]

The room-temperature resistivity of the as-deposited films was measured by use of a four-point probe. The films deposited using ethanoic anhydride, ethanoic acid, and water all failed to produce a reading, indicating that these films were "insulating" in the as-deposited state. This relates to a sheet resistance in excess of 2000 Ω/□. Films deposited using methanol had a resistivity of approximately 4×10^{-2} Ω cm, and those deposited using ethanol had a resistivity of approximately 8×10^{-3} Ω cm. These results are in accordance with the idea that reduction of stoichiometric colorless WO_3 changes its electrical conductance from behaving as an insulator to becoming more conductive as it progressively reduced, giving an increasingly intense-blue coloration.[33]

Measurement of water-droplet contact angles was made on each of the films. The films produced by reaction of WCl_6 and ethanoic acid had contact angles of around 70° as-deposited and of 60° after UV irradiation, while those deposited using ethanoic anhydride had angles of 40° before irradiation and 30° after. The films produced using methanol had contact angles of 25°, which after irradiation fell to 20°. The films deposited using ethanol and water had similar contact angles as-deposited, approximately 10°, but after irradiation these became ∼7° for the water deposited films but only 2.5° for ethanol. Contact-angle measurements on tungsten oxide films deposited via AACVD using tungsten hexaphenoxide gave values of between 50 and 60° before irradiation and 5−20° after irradiation.[23] The contact-angle measurements before irradiation are a measure of the surface hydrophilicity, which is modified by a number of factors such as chemical composition, level of oxidation (presence of W═O terminal bonds), surface morphology, and perhaps water content. As the film is reduced the film will become more hydrophilic,[34] which is why it is not surprising the contact angle of the blue methanol and ethanol deposited films are low, although the low contact angle of the as-deposited water film is surprising and may relate to increased water content or presence of surface −OH species, although these were not obvious by Raman. The decrease on UV irradiation is relatively small in all cases, except that for the film deposited using ethanol where the film becomes extremely hydrophilic after irradiation. This was thought surprising because the lowering of the contact angle is associated with a reduction of WO_{3-x} and yet the color of this film and the XPS data show that it is already the most reduced of all the as-deposited films.[34]

Functional Properties. The functional properties of the films, namely, photochromism and photocatalysis, were examined. It was reported by Gavrilyuk that WO_3 films oxidized at elevated temperatures ($T > 500$ °C) for longer than 30 min lose practically all photochromic sensitivity, probably due to an increase in crystallite size.[34] The as-deposited films prepared in this study were also oxidized at 400 °C for a period of 12 h. The oxidative process did not change the Raman or XRD patterns of the films deposited using ethanoic anhydride, ethanoic acid, water, or methanol as the reactants. The films deposited using ethanol showed a change in the XRD with the preferred orientation diminishing. No change was apparent in the Raman pattern, and therefore an SEM image was used to examine the surface (Figure 9). Compared to the SEM image before oxidation (Figure 2) it is apparent that the process has sintered the needles to a small degree, leading to shorter, broader needle formations. There is also some evidence for the formation of small cubic aggregates of crystallites. XPS was also used to analyze the oxidized film, and the surface displayed only

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Figure 9. SEM of film deposited from WCl_6 and ethanol at 625 °C, oxidized at 400 °C for 12 h (scale bar reconstructed for clarity).

one tungsten environment with $W4f_{7/2}$ 35.3 eV, indicating that the film was fully oxidized (no W^{5+} or W^{4+}) WO_3.

The samples to be examined for photocatalysis were pre-irradiated under a 254-nm lamp for 1 h before having the stearic acid substrate spin coated onto them. The films were "aged" using a 365-nm lamp and the photodecomposition of stearic acid followed over time using FT IR spectroscopy. It was found that only the oxidized films deposited from WCl_6 and ethanol displayed any photodecomposition of the stearic acid with all of the other films being comparable to uncoated glass. After 12 h of irradiation, 35% of the stearic acid had been decomposed with uncoated glass showing a zero change in the amount of stearic acid. The result for the active films are in accordance with WO_3 films deposited using AACVD from $W(OPh)_6$[23] and from the polyoxotungstate $[n\text{-}Bu_4N]_2[W_6O_{19}]$.[35] This photoactivity has previously been correlated to being as active as TiO_2 deposited using similar CVD techniques.[23]

The photochromic response was examined by taking freshly oxidized films and measuring the absorption spectra in the visible region, exposing the films to 254-nm UV radiation and then remeasuring the absorption spectra. It was found that only one type of film demonstrated a measurable photochromic response, those deposited from the reaction of WCl_6 and ethanoic anhydride, which showed a change in optical density of ~0.3 absorption units at 633 nm after 1 h irradiation. Further irradiation produced no increased coloration in any of the films. The saturation time for maximum coloration in the ethanoic anhydride films was not determined. The results from this study were surprising, given the results of the photocatalysis experiments. The ethanoic anhydride deposited films showed no photocatalytic activity but displayed a photochromic response, which is initially incongruous, although it can be explained as being due to the pre-irradiation prior to the photocatalysis tests reducing the film and deactivating it. More difficult to explain is the lack of a photochromic response in the oxidized films deposited using ethanol as the reactant. Tungsten oxide photocatalysis is rarely mentioned in the literature, with the prevailing view being that is photoinactive, but many of WO_3 films produced using other CVD methodologies have demonstrated remarkable activity.[18,23,35] By assumption that the mechanism put forward by Gavrilyuk[34] for photochromic coloration is the "byproduct" of photocatalysis then it is difficult to understand this separation of effects. In fact Gavrilyuk claims that the "use" of water as a substrate for photochromism (as atmospheric humidity would have provided for the photochromism experiments) gives poor results relative to the use of an organic, such as methanol or by extension even stearic acid (as was the case in the photocatalysis experiments). It is possible that the films deposited using ethanol have a much higher surface area than the films deposited using other reactants due to their needlelike microstructure. A possible explanation is that the reduction from W^{6+} to W^{5+} that takes place during photoirradiation of WO_3 is matched by an immediate reduction of W^{5+} to W^{4+}, removing the formation of W^{6+}/W^{5+} (or W^{5+}/W^{4+}) color centers or that there is an immediate reoxidation of W^{5+} to W^{6+} with no "trapping" of reduced tungsten species in the bulk. XPS analysis of ethanol films irradiated with 254-nm UV radiation for 2 h (in air) showed no evidence of W^{4+} species but this evidence is inconclusive.

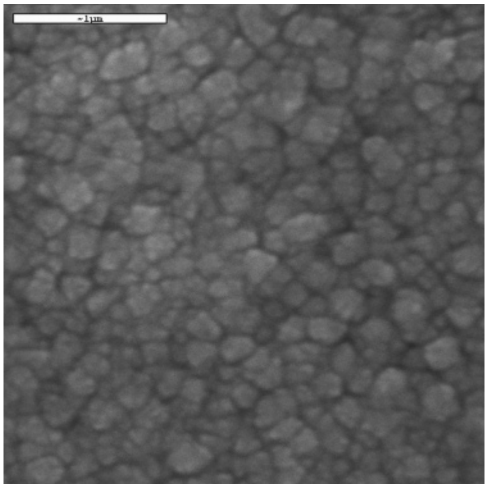

Figure 10. SEM of film deposited from WCl_6 and ethanoic anhydride at 450 °C.

Effect of Changing Reaction Conditions. Reaction conditions were examined for films deposited from the CVD of WCl_6 with ethanoic anhydride (Table 2). The deposition temperature was decreased while maintaining the molar ratio (1:25 W:reactant), and it was found that the rate of film growth changed from 1000 to 200 nm/min on going from 625 to 450 °C. Below 450 °C, no deposition was seen in the 1-min deposition time. The films deposited at 450 °C had identical XRD patterns and Raman spectra to those deposited at 625 °C although the Raman had much lower intensity peaks and evidence of amorphous character. An SEM image (Figure 10) shows that the crystallites in a film deposited at 450 °C are smaller than those deposited at 625 °C (Figure 1) (800 and 1100 Å as determined by the Scherrer equation).

The next parameter to be examined was the effect of plain flow on the deposited films. At a substrate temperature of 500 °C and with an identical molar amount of reactants flowing through the reactor, the plain flow was varied between 20 and 2 L/min. At 10 L/min, thick (~725 nm) yellow films were deposited. Increasing the flow rate to 20 L/min effectively stopped film formation, while reducing the

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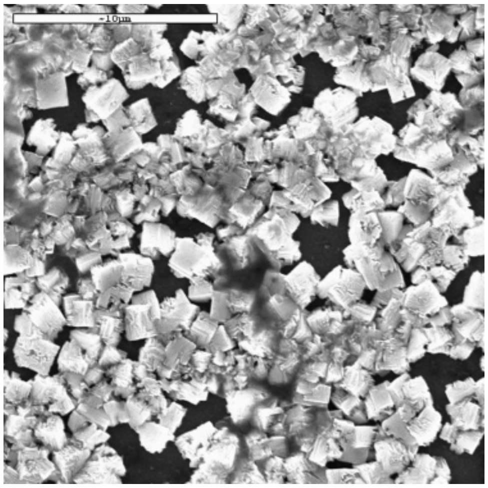

Figure 11. SEM of film deposited from WCl_6 and ethanoic anhydride at 500 °C and a plain flow rate of 5 L/min.

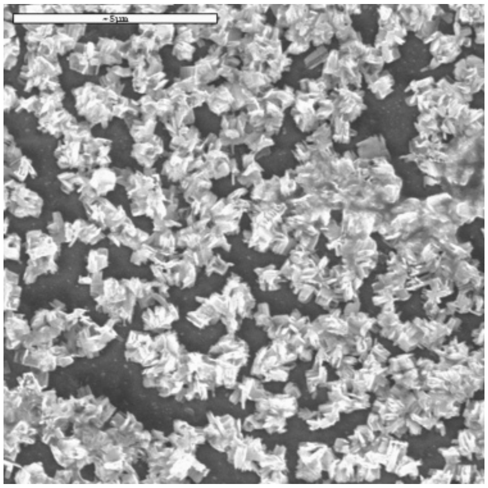

Figure 12. SEM of film deposited from WCl_6 and ethanoic anhydride at 500 °C and a plain flow rate of 2 L/min.

plain flow caused thinner films to be deposited (as determined visually and by Si breakthrough measurement using WDX). In all cases, the films gave XRD patterns matching those of monoclinic WO_3 and had identical Raman spectra although in both analyses the intensities were much diminished either due to reduced film thickness, reduced crystallinity, or a combination of both. SEM analysis highlights the diminishing surface coverage with decreasing plain flow at 5 (Figure 11) and 2 L/min (Figure 12).

It is interesting that such high flow rates are required to obtain films using the WCl_6 + reactant system. WO_3 deposition has been achieved using $WOCl_4$ and ethylethanoate under more "normal" conditions of ~2 L/min total flow with a similar molar amount of reactants,[18] and in fact, this is the only system encountered in our group that requires such a growth regime. The lack of deposition at very high flow rates is attributed to the low residence time of species in the reactor.

The final parameter examined was the effect of reactant ratio. At a substrate temperature of 500 °C, the WCl_6:ethanoic anhydride ratio was varied between 1:10 and 1:125. At a reactant ratio of 1:30, relatively thick (475 nm) films were deposited. Increasing the reactant ratio to 1:125 led to the deposition of thinner films (WDX Si breakthrough), as did decreasing the reactant ratio to 1:10. XRD and Raman analysis showed that in each case the films were monoclinic WO_3. Changing the reactant ratio only had the effect of reducing the film thickness, but the chemical composition remained the same.

Conclusions

The APCVD reaction of WCl_6 with ethanoic anhydride, water, or ethanoic acid deposits crystalline films of fully oxidized monoclinic WO_3 at a substrate temperature of 625 °C. The films deposited using ethanoic anhydride or ethanoic acid as the reactant have similar morphologies with cubic crystallites formed, whereas the films deposited using water have a platelike morphology. The APCVD reaction utilizing methanol or ethanol at a substrate temperature of 625 °C produces crystalline films of reduced WO_{3-x} (where $x \approx 0.07$ for methanol and $x \approx 0.35$ for ethanol), which have XRD structures matching that of monoclinic tungsten oxide although in the case of deposition using ethanol there is preferred orientation in the $\langle 020 \rangle$ plane. The films deposited using ethanol as the reactant had a needlelike morphology, orientated parallel to the substrate, whereas the films deposited using methanol had a morphology composed of an underlying mat of "wires" with large cubic crystallites growing out of the substrate surface. The change in morphologies with changing reactant was striking. Analysis of the films' functional properties showed that films deposited using ethanoic anhydride displayed photochromic behavior after oxidation at 400 °C but no photocatalysis. This is explained by the experimental conditions used to measure the photocatalysis. The films deposited using ethanol, subsequently fully oxidized at 400 °C, showed pronounced photocatalytic activity, on par with titanium dioxide, but had no photochromic response. Experiments carried out on deposition parameters for the reaction of WCl_6 and ethanoic anhydride showed that flow rates through the reactor were unusually high, compared to other APCVD reactions examined. At lower flow rates, the rate of deposition was extremely slow. Changes in substrate temperature between 450 and 625 °C showed that the phase of crystalline WO_3 deposited did not change only the level of crystallinity. Changes in reactant ratio also caused no discernible change in film composition.

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