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Metallo-organic deposition of tungsten oxide films from alkylammonium tungstate solutions

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This paper describes a simple and inexpensive metallo-organic deposition (MOD) process for forming electrochromic tungsten oxide (WO_3) films on glass. The thin films of WO_3 were made by air firing (500–700° C) films from xylene/2-propanol solutions of bis-(di-*n*-octylammonium) tetratungstate, $[(n\text{-}C_8H_{17})_2NH_2]_2[W_4O_{13}]$. The process coats glass with undoped films ranging in colour from faint yellow to dark brown, and can be used to make gradients of these colours. The colour is determined by the firing parameters and results from residual carbon and tungsten suboxides in the film due to incomplete firing. Increased firing temperatures or longer firing times removes the carbon and produces films with higher crystallinity. Electrochemical doping with acid (H^+) switches the colour gradient films to a uniformly blue colour.

1. Introduction

Electrochromic materials are substances which change their colour in response to an externally applied electrical potential [1]. They are of interest for use as glass coatings for producing windows with controllable light transmission. Such windows can be used for 'privacy control' and for reducing the solar heat load in automobile passenger compartments. Solar generated heat is becoming an increasing problem as the amount of glass used in modern vehicle designs increases.

Tungsten oxide, WO_3, is an electrochromic material that shows promise for automobile applications. It is normally a faint yellow (thin films are essentially colourless), but when electrochemically doped with protons or alkali metal ions, it turns blue [2]. By controlling the extent of doping, colouration ranging from faint to deep blue can be achieved. Tungsten oxide films in the reduced state have a strong and broad absorption band in the visible range of $\lambda >$ 500 nm which extends into the near infrared range ($\lambda >$ 900 nm). In the oxidized state, the films become transparent. Tungsten oxide is considered to be the best of the well characterized electrochromic materials [1].

Typically, WO_3 films are formed using vacuum deposition techniques [3, 4] such as chemical vapour deposition (CVD) [5] or plasma enhanced chemical vapour deposition (PE–CVD) [6]. The equipment is expensive, both to purchase and operate, and cannot be used to coat large areas easily. Metallo-organic deposition (MOD) offers an alternative to vacuum processes for the preparation of thin films [7, 8]. In this process, films of metallo-organic compounds are applied to the substrate of interest. The films are then pyrolysed, which removes the organic material, leaving an inorganic film on the substrate surface. Ideally, the metallo-organic compound should be stable to air and water and should have a long shelf life. It must also be soluble in a solvent which wets the substrate.

In this paper we describe the development of a metallo-organic deposition process for forming electrochromic WO_3 films. Suitable metallo-organic compounds are identified and processing parameters determined. The use of processing parameters to modify film characteristics is also discussed.

2. Experimental details

2.1. *Preparation of Bis(di-n-octylammonium) tetratungstate*, $[(n\text{-}C_8H_{17})_2NH_2]_2[W_4O_{13}]$

Method 1. 60.9 g (250 mmol) of di-*n*-octylamine, $(n\text{-}C_8H_{17})_2NH$, were added to a 1 L round bottom flask containing a stirring bar and 400 mL of water. Addition produced a solid amine hydrate which melted upon heating. Once melted, the mixture was allowed to cool until the hydrate completely resolidified on the surface of the water. 29.9 g (120 mmol) tungstic acid, H_2WO_4, were poured onto the solid hydrate, a condenser was attached, and the mixture was refluxed with vigorous stirring for 1 h. (*Note*: without strong stirring, the mixture will often decompose to an insoluble blue material.) While still hot, the contents were isolated using a separatory funnel; the more dense tungstate melt settled to the bottom. After separation, the crude product was allowed to solidify and any remaining liquids decanted.

The product was purified by adding boiling water to the crude material, which melted. As the mixture cooled, the product solidified below the water. Amine hydrate floated to the top and was decanted with the

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water. This was repeated until little or no amine was extracted. The product was then dissolved in 50 : 50 2-propanol : xylene, filtered through course filter paper, filtered through a 0.2 μm pore size polypropylene membrane filter, and heated to dryness (120° C for 2 h). This step was repeated, leaving a glassy, yellow, transparent product. Elemental analysis: found – 28.4%C, 46%W; calc. – 26.9%C, 52%W.

Method 2. 10.0 g (40.0 mmol) H_2WO_4 was added to a 300 mL flat bottom boiling flask containing a stirring bar and 120 mL methanol. 20.0 g (82.8 mmol) $(C_8H_{17})_2NH$ was added. Water was added (about 60 mL) and the mixture immediately became cloudy with the formation of oily-yellow particles. After two hours of refluxing, the now milky white solution was allowed to cool. The alcohol and water were distilled off, and the remaining solid was purified in the manner described in Method 1.

2.2. *Film preparation*

Thirty percent solutions (in 50 : 50 2-propanol : xylene) of $[(n\text{-}C_8H_{17})_2NH_2]_2[W_4O_{13}]$ were filtered through 0.2 μm pore size polypropylene membranes. The solution was spun cast at 2000 r.p.m. for 30 s onto 5 cm × 5 cm indium tin oxide (ITO) or fluorine doped tin oxide (FTO) coated glass. (So that electrical contact could be made with the ITO or FTO, a small segment of the film was removed by wiping with a tissue soaked in 2-propanol). Oxide films were produced by firing in an oven at 500 or 600° C for times ranging from 5 to 20 min.

2.3. *X-ray diffraction*

Diffraction patterns were obtained by preparing ITO glass with 5 layers of MOD-produced WO_3. In this case, each coat was spun onto the substrate followed by a 5 min firing at 500° C. After the layers were applied, a diffraction pattern was obtained. The specimen was then heated for 5 min at 600° C and a second pattern obtained. A final diffraction pattern was obtained after a 5 min firing at 700° C.

2.4. *X-ray photoelectron spectroscopy*

X-ray photoelectron spectroscopy (XPS) depth profiling experiments were performed on a Surface Science Instruments SSX-101 instrument equipped with differentially pumped Leybold–Heraeus ion source. Data were acquired using a monochromatic AlK_α X-ray source with a spot size of 300 μm. A hemispherical analyser with a pass energy of 150 eV provided an energy resolution of 1.5 eV. Depth profiling was performed using a 4 kV Ar^+ ion beam rastered over a 1 mm by 1 mm area. Elemental compositions were calculated by measuring the area under the photoelectron transition, and correcting this value using Scofield cross section [9] and inelastic mean free path [10] data.

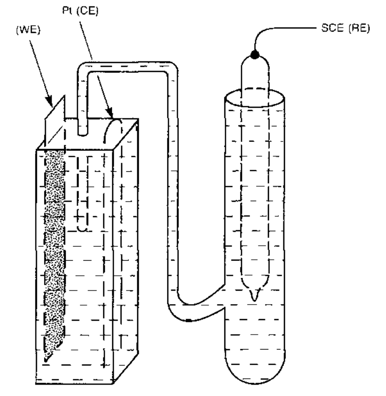

Fig. 1. The spectroelectrochemical cuvette cell showing the working electrode (WE), the saturated calomel reference electrode (RE), and the platinum counter electrode (CE).

2.5. *Electrochemical and spectroelectrochemical experiments*

A classical 3-electrode cell was used for the electrochemical measurements. The WO_3 films were prepared by the MOD method described above. Substrates used were ITO or FTO coated glass. A saturated calomel reference electrode (SCE) and a platinum spiral coil counter electrode were used. The electrochemical equipment included an EG&G PAR Potentiostat model 173, Universal Programmer model 175, and a Hewlett-Packard recorder.

For spectroelectrochemical measurements a 3-electrode cuvette cell with 1 cm path length (Fig. 1) was used. The electrolyte was 0.5 M H_2SO_4 in tri-distilled water. The cell was placed in the sample chamber of a Perkin-Elmer Lambda-9 spectrometer and the *in situ* transmittance spectra were recorded with the electrode polarized at each potential for 5 min.

3. Results and discussion

The MOD process requires a metallo-organic compound which is soluble in a volatile organic solvent. Previously developed MOD processes have used carboxylate salts for depositing transition metal oxides [7, 8]. However, a successful synthesis of tungsten carboxylates has never been reported. A successful MOD process for WO_3 production using metal alkoxides has been reported [11]; however, alkoxides tend to be water sensitive and are usually prepared from WCl_6, which must be handled in a controlled atmosphere. Therefore, an alternative approach employing alkyl ammonium salts of tungstic acid was used in this study.

Of the alkyl ammonium salts we examined, bis(di-*n*-octylammonium) tetratungstate is the simplest to synthesize and is highly soluble in a xylene/2-propanol mixture. Good films were cast from solutions of ∼ 1 part each of the product, xylene, and 2-propanol. This solution composition was used to prepare all the films described in this report.

The elemental analysis results show that the reaction product between $(n\text{-}C_8H_{17})_2NH$ and H_2WO_4 does not yield a simple tungstate, such as

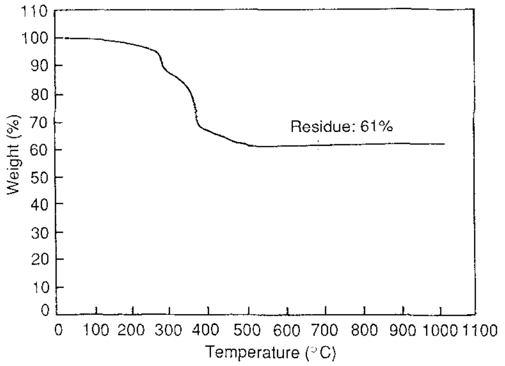

Fig. 2. Thermogravimetric analysis of $[(n\text{-}C_8H_{17})_2NH_2][W_4O_{13}]$.

$[(n\text{-}C_8H_{17})_2NH_2]_2[WO_4]$ (expected results for this compound would be 52.4%C and 25%W). Thermogravimetric analysis (TGA) results (Fig. 2) confirm that the product is a tetratungstate. The pyrolysis product, WO_3, would remain as approximately a 32% residue for the simple tungstate instead of the 65% WO_3 expected from a tetratungstate. The 61% WO_3 residue found by TGA is reasonable considering that some W-containing material is likely to be carried off during volatilization of the tetratungstate. The formation of a tetratungstate is the result of condensation reactions and there may be higher polymetalates [12] present since elemental analysis indicates that the product is rich in tungsten.

During film firing studies we noted that the resultant film colour was sensitive to the conditions employed. When fired in air for 5 min at 500° C, the films were a deep brown. Longer firing times caused the colour to fade until after 20 min the films are a faint yellow. Films fired in air at higher temperatures such as 600° C produced faint yellow films at shorter firing times (5 min). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to examine films fired at different times and temperatures in order to determine why film colour is sensitive to these parameters.

The XRD pattern of a specimen fired at 500° C for 5 min contained two broad peaks at 24.0° and 29.8°. Both these peaks sharpened and intensified after the 600° C firing and additional peaks appeared at 49.8°, 61.4°, and 55.3°. All peaks were sharper and more intense after firing at 700° C for 5 min. These lines correspond to the diffraction pattern of orthorhombic WO_3 and indicate that with longer firing or firing at higher temperatures, the WO_3 either becomes more crystalline, or that the initially formed (darker) films contain suboxides of WO_3.

The elemental compositions of films as a function of depth were determined by combining XPS with argon ion sputtering. The resultant depth profiles are displayed in Fig. 3 for specimens fired at 700° C for 5 min (light yellow) and at 500° C for 5 min (dark brown). The light yellow film, Fig. 3a, contains only tungsten and oxygen. Determination of the chemical form of tungsten and oxygen in the film is impossible due to ion bombardment induced reduction of the film during argon ion sputtering. In addition, the sputter process preferentially removes oxygen from the film which alters the oxygen to tungsten ratio from the expected 3 : 1 to a value near 1 : 1. However, the depth profile of the MOD film is identical to one obtained from a WO_3 standard, suggesting that the compositions of both films are similar. The oxygen to tungsten ratio for the specimen fired at 500° C was less than 1 : 1 (see Fig. 3b). This suggests that a tungsten rich film is formed at low firing temperature (or short firing time). The film is probably a suboxide of WO_3, formed due to incomplete reaction of the film. Furthermore, the dark film also contains significant amounts of carbon in addition to tungsten and oxygen. The presence of carbon in the film is the most likely reason this film is coloured dark brown. Since this specimen was fired at a lower temperature and for a shorter time, the carbon is probably present because of incomplete pyrolysis of the metallo-organic compound.

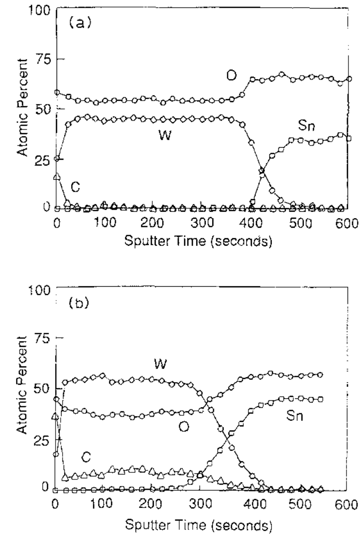

Fig. 3. XPS depth profiles of tungstic oxide MOD films fired using the following conditions: (a) 5 min at 700° C in air; (b) 5 min at 500° C in air. Specimen b contains significant amounts of residual carbon film due to incomplete firing.

The ability to control the film colour by changing the processing conditions can be used to produce some interesting effects. For example, yellow to brown colour gradients can be produced across a piece of glass by inducing differences in either the time of firing, or the temperature. A 5 cm × 5 cm piece of ITO coated glass was placed on a quartz holder so that one portion of it (2 cm length) extended over the edge of the holder. The quartz acts as a heat sink which keeps the film cooler (the temperature difference was not determined) where the holder and film contact. When placed in an oven at 500° C, the extended edge heated faster and quickly darkened. After 15 min, the extended edge became a faint yellow, while the portion that rested on the quartz heat sink was dark. It is possible that large glass parts could be given colour gradients through many different processing techniques: (i) by making use of the temperature gradients that occur in ovens (the cooler zones would produce a darker region); (ii) using different exposure times, the lighter region would enter the oven first, the part

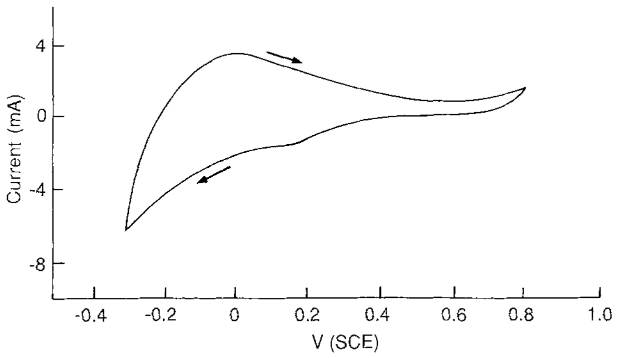

Fig. 4. Cyclic voltammogram of a WO_3 film deposited by MOD on an ITO coated glass substrate. (Solution: 0.5 M H_2SO_4 (aq), scan rate: 50 mV s^{-1}).

would be rotated, then the dark region would exit first; (iii) using heat shields, such as screens; or, (iv) by using heat sinks.

A cyclic voltammogram of the WO_3 film in 0.5 M H_2SO_4(aq) is shown in Fig. 4. U.v.-visible spectra of both the faint and dark zones with the electrode polarized at −0.7 V and at 0.7 V (SCE) are shown in Figs 5 and 6, respectively.

The cyclic voltammogram of the WO_3 film on the fluorine doped tin oxide (FTO) coated glass surface in 0.5 M H_2SO_4 solution (aq.) (Fig. 7) is very similar to those obtained with WO_3 films made by reactive sputtering [13], chemical vapour deposition [14], or evaporation technique [15]. The electrochemical reactions of the WO_3 film made by the present MOD method, thus, correspond to the following reaction:

$$WO_3 + xH^+ + xe^- \Leftrightarrow H_xWO_3 \qquad (1)$$

The u.v.-visible spectra of the lighter portion of the film, produced by subjecting the film to higher temperatures during the film preparation, shows a maximum in transmittance around 500 nm. The darker portion of the film, however, shows a maximum around 1000 nm suggesting that the film still contains some unburned organic materials due to exposure of this portion of the film to relatively milder pyrolysis conditions during film preparation. This is in agreement with the XPS results.

Both the darker and lighter portions of the film showed optical switching effects by switching the potential between the anodic and the cathodic limits (Figs 5 and 6). Thus, by varying the temperature across the surface during film preparation, one may obtain WO_3 films with colour gradients that exhibit electrochromic properties. The optical contrast between the reduced and the oxidized state (Figs 5 and 6) is quite low compared to the contrast obtained with the sputtered film [1]. However, optimizing the preparation procedure improves the contrast. In Fig. 7, the spectra of the reduced and the oxidized WO_3 film made by optimized MOD conditions are shown. This film was prepared identically to the film from which Figs 5 and 6 were derived, except that it was fired for 25 instead of 5 min at 500° C. The transmittance of the optimized film was found to vary from 15% in the coloured state to 95% in the bleached state (Fig. 7).

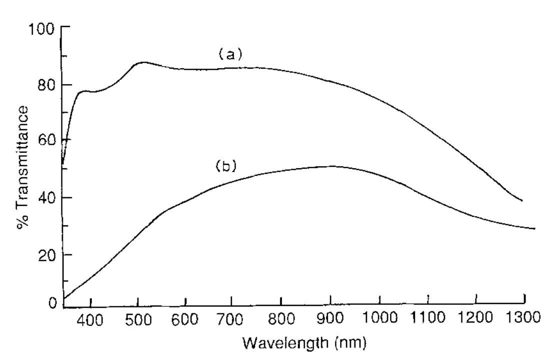

Fig. 5. *In situ* u.v.–vis.–n.i.r. spectra of the light portion of the WO_3 film held at +0.7 V (a) and −0.2 V (b) (SCE) in 0.5 M H_2SO_4 (aq).

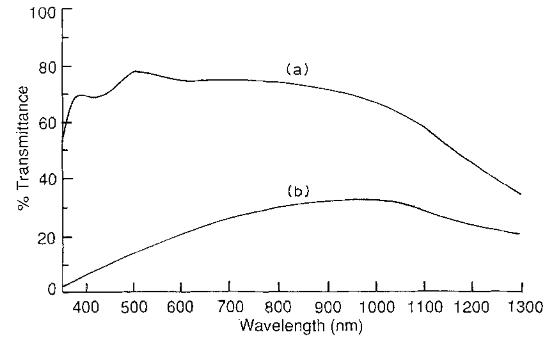

Fig. 6. *In situ* u.v.–vis.–n.i.r. spectra of the dark portion of the WO_3 film held at +0.7 V (a) and −0.2 V (b) (SCE) in 0.5 M H_2SO_4 (aq).

4. Conclusions

1. A metallo-organic deposition (MOD) technique was successfully developed to produce electrochromic tungsten oxide films which offer the potential for inexpensive controllably darkening windows and mirrors.
2. Processing conditions can be controlled to alter the undoped colour of the films. Firing the MOD compound in air at 500–700° C produces films which vary from yellow to brown with:
   (a) lower temperatures or shorter firing times leading to darker colour due to increased residual carbon in the film and suboxides of tungsten.
   (b) temperature gradients leading to colour gradients.

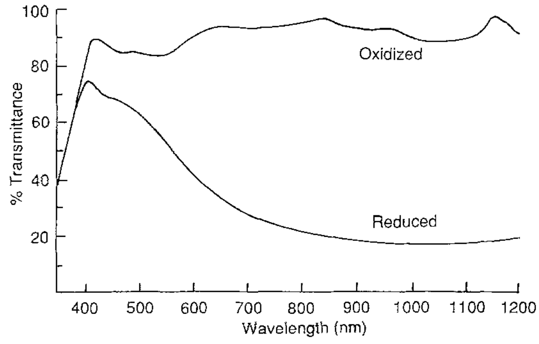

Fig. 7. *In situ* transmitance spectra of a WO_3 film made by MOD in the oxidized state on ITO coated glass (+0.8 V/SCE) and in the reduced state (coloured) (−0.2 V/SCE). The electrolyte was 0.5 M H_2SO_4 (aq).

3. When placed in a classical three-electrode electrochemical cell, the films can be doped with H^+ which switches them to a uniform blue colour.

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