

Observation of non-ideal lithium insertion into sputtered thin films of tungsten oxide

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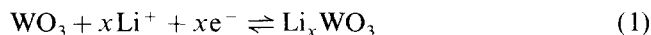
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Abstract

The electrochromic colouration and electrochemical behaviour of sputtered thin films of tungsten oxide (WO_3) in a lithium-containing electrolyte have been investigated. We found the behaviour to be extremely sensitive to the deposition conditions. In particular, we have produced WO_3 thin films over a wide range of sputtering conditions, and found that in some cases, large amounts of lithium can be inserted irreversibly with no change of colouration. It is found that material showing this effect is predominantly produced by sputtering from a tungsten metal target. Different experiments have been carried out in order to isolate the mechanism responsible for this irreversible intercalation, and the indications are that a single phase of Li_xWO_3 is not formed as is usually expected, but instead we most probably see a chemical reaction of lithium with interstitial oxygen to form a two-phase compound. Our findings may have implications for the manufacture of tungsten oxide thin films for electrochromic windows.

1. Introduction

Thin films of tungsten oxide (WO_3) on transparent conductive oxides (TCOs) have been known for many years to produce colouration when lithium ions and electrons are co-inserted to form a non-stoichiometric tungsten compound [1]. This is usually written



where the WO_3 is colourless and the Li_xWO_3 is blue. A potential application of this material is the manufacture of variable transmission windows [2]. The majority of electrochromic devices based on tungsten oxide use the same basic arrangement that has been described many times elsewhere [3–7] and so will not be repeated here. It is sufficient to note that in most cases the counter electrode, often called the ion storage layer, is the element that limits the colouration depth. This is mainly due to the fact that the majority of materials used in this role have a smaller charge capacity than the tungsten oxide [8]. It is therefore important for the tungsten oxide to be as near ideal as possible, which for the purpose of this paper is taken to mean having maximum electrochromic efficiency as well as being completely reversible to charge insertion and extraction.

Electrochromic colouration has been measured by many other workers [9–20]. The most physically meaningful measurement when discussing electrochromic colouration is to determine the absorption over a range

of wavelengths induced in the films as a result of the charge inserted. It is, however, usual practice to measure the transmission change and calculate an optical density OD using

$$OD = \log_{10} \left| \frac{T_0}{T(q')} \right| \quad (2)$$

where T_0 is the initial transmission and $T(q')$ is the measured transmission after the charge has been inserted. In practice many workers measure the change in transmission at just one wavelength for convenience, which can have the effect of giving misleading values of OD and hence of the electrochromic efficiency. In our measurements, we have used a weighted transmission for $T(q')$ where

$$T(q') = \frac{\int [T_{\text{data}}(\lambda) C_{\text{weight}}(\lambda)] d\lambda}{\int C_{\text{weight}}(\lambda) d\lambda} \quad (3)$$

$T_{\text{data}}(\lambda)$ are the measured transmission data, and $C_{\text{weight}}(\lambda)$ is the weighting factor to try to obtain consistent and reliable results. We have used both the eye response and the solar irradiation spectrum for the weighting factor at different times, and find that either one can be used with confidence.

In this study we have used a variety of different deposition techniques, and in general we find results

which are similar to those previously reported [9–20], but we find that under certain deposition conditions, we can obtain behaviour which does not obey the ideal Beer–Lambert law [21]. In this paper, we describe the deposition conditions which yield this non-ideal behaviour and propose a simple model that can explain all the observed behaviour.

2. Experimental details

Measurement of the electrochromic behaviour involved measurement of the white light transmission of the WO₃ thin film as a function of charge insertion. This was accomplished by using a tungsten halogen white light source, with a fibre optic bundle to take the light directly into the electrochemical cell. Another fibre bundle took the light that had been transmitted through the sample to a detection system. This comprised a Spex 1681 single grating monochromator, with a ‘two-colour’ Si photo-diode/PbS photoconductor as a detector. The monochromator was equipped with a grating turret holding two different gratings to enable us to measure spectra over a wavelength range of approximately 400 nm to 2500 nm. The gratings were one of 600 grooves mm^{−1} blazed at 750 nm, and another of 300 grooves mm^{−1} blazed at 1700 nm. The spectrometer control and data acquisition system was in turn controlled by a personal computer, which allowed storage and manipulation of the transmission data.

A Schlumberger 1286 electrochemical interface (ECI) was used to control the potential of the WO₃ working electrode (WE) relative to a lithium metal reference electrode (RE). Lithium metal was also used as the counter electrode (CE). The electrolyte used was a carefully dried solution of 0.5 M lithium triflate (LT) in propylene carbonate (PC). In this work we have used the galvanostatic mode of the ECI to allow accurate measurement of the amount of charge inserted into the WE under a constant current. We were very careful to monitor and limit the potential of the WE during charging and discharging of the WO₃ to prevent undesirable side reactions from occurring.

Most of the thin films of WO₃ used in this work were deposited by r.f.-diode sputtering onto transparent conducting substrates of ITO of nominal sheet resistance 20 Ω □^{−1}, under a variety of pressures and reactive gas compositions from both oxide and metal targets. In addition, further films were deposited by reactive d.c. magnetron sputtering for comparison. All the films discussed in this paper can be divided into the two following broad groups.

Group I. Polycrystalline material r.f.-sputtered from a tungsten target, plus both polycrystalline and amorphous material r.f.-sputtered from a tungsten oxide target.

Group II. Amorphous material r.f.-sputtered or d.c.-magnetron sputtered from a tungsten target.

It is obviously possible to produce a wide variety of properties by varying deposition parameters within the two groups, but for the purpose of this paper, we find that it is sufficient to limit our subdivisions to these two groups.

3. Results

Figure 1(a) shows the results of measurement of the electrochromic behaviour of a series of films from Group I, with details of the sputtering parameters given in the caption. Note that the only parameter which is varied is the deposition time, yielding a range of thicknesses. In all cases the films were transparent, with initial solar transmission T_{sol} greater than 85% when referenced to the base glass. We see that for all the films measured, as the charge is inserted there is an initial linear increase in OD , followed by saturation. The initial linear increase is to be expected from the Beer–Lambert law, and the slope of this characteristic gives the electrochromic efficiency α . The OD saturates at different values depending on the thickness of the WO₃ film. These same data are plotted in Fig. 1(b) against mole fraction of lithium (x in Li_{*x*}WO₃), calculated according to

$$x = \frac{q'M}{F\rho t} \quad (4)$$

where q' is the charge inserted per unit area, ρ and M are the density and molecular mass of the WO₃, F is Faraday's constant, and t is the film thickness. It can be seen from Fig. 1(b) that the saturation appears to be connected with a specific molar fraction of lithium independent of the film thickness.

Figure 2(a) shows the corresponding data for a set of films from Group II. Again the only variable parameter is deposition time, but we see a completely different type of behaviour in this case. Initially, the inserted charge causes no observable colouration, but begins to colour the film after insertion of an amount of charge related to the film thickness. Further similar experiments show that this is also dependent upon preparation conditions in a non-trivial way. Figure 2(b) illustrates this for this particular series of films. We have plotted OD against the calculated molar fraction of lithium. The characteristics for the films of different thickness can be seen to lie roughly on the same line indicating that the amount of non-colouring charge also seems to be related to a specific molar fraction.

Figure 3 shows the development of the $OD(q')$ characteristic as the charge is cycled in and out. The data

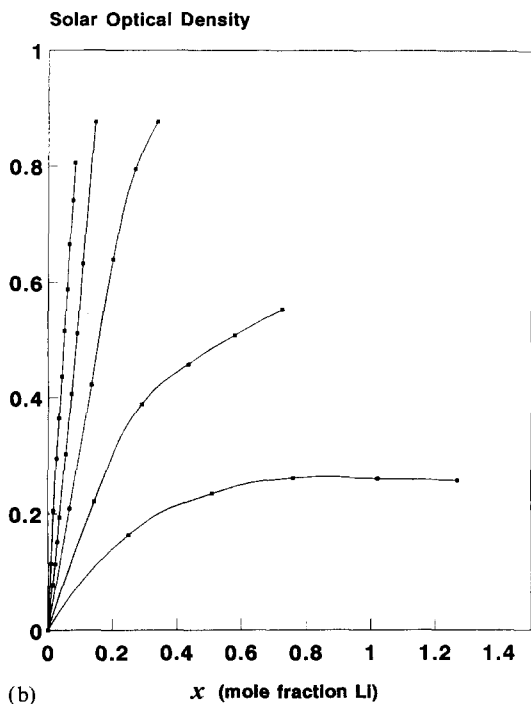
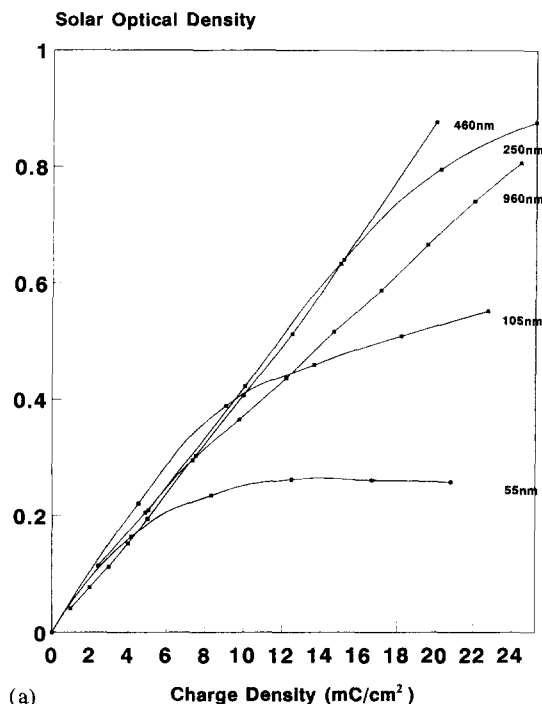


Fig. 1. Solar-weighted OD for Group I WO_3 plotted: (a) as a function of inserted charge per unit area, and (b) against molar fraction of lithium x . The film thicknesses are as shown in (a). The films were r.f.-diode sputtered at 3.0×10^{-2} mbar in an atmosphere of Ar/10% O_2 at an approximate growth rate of 0.1 nm s^{-1} .

shown here were obtained from an amorphous film grown by d.c.-magnetron sputtering, in order to illustrate the similarity with the amorphous films grown by r.f. reactive sputtering. We inserted charge up to ap-

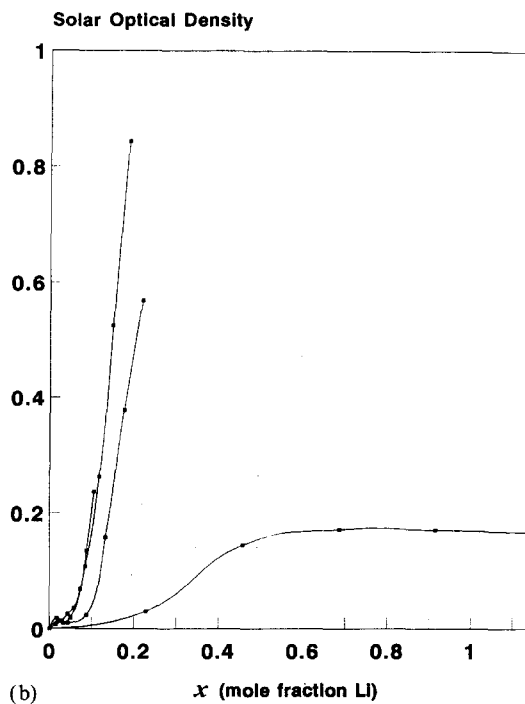
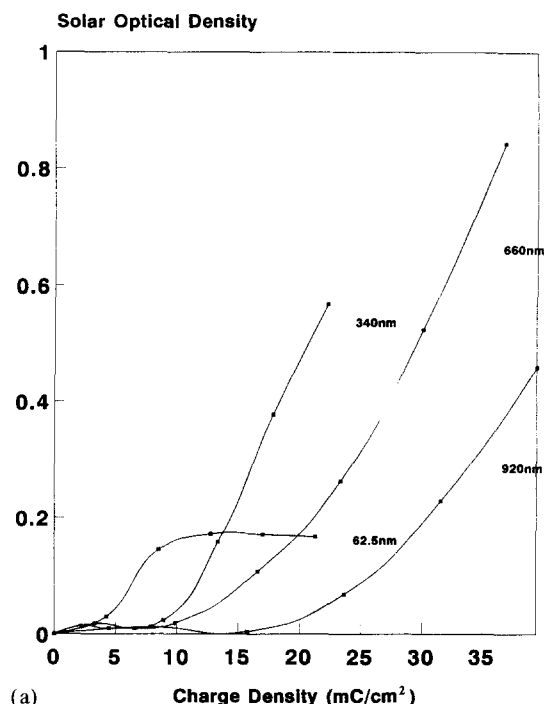


Fig. 2. Solar-weighted OD for Group II WO_3 plotted: (a) as a function of inserted charge per unit area, and (b) against molar fraction of lithium x . The film thicknesses are as shown in (a). The films were r.f.-diode sputtered at 3.0×10^{-2} mbar in an atmosphere of Ar/1% O_2 at an approximate growth rate of 0.09 nm s^{-1} .

proximately 75 mC cm^{-2} , which was required to produce an acceptable OD . The direction of current flow was then reversed in order to extract the charge again. The OD is seen to rapidly reduce to zero at a residual

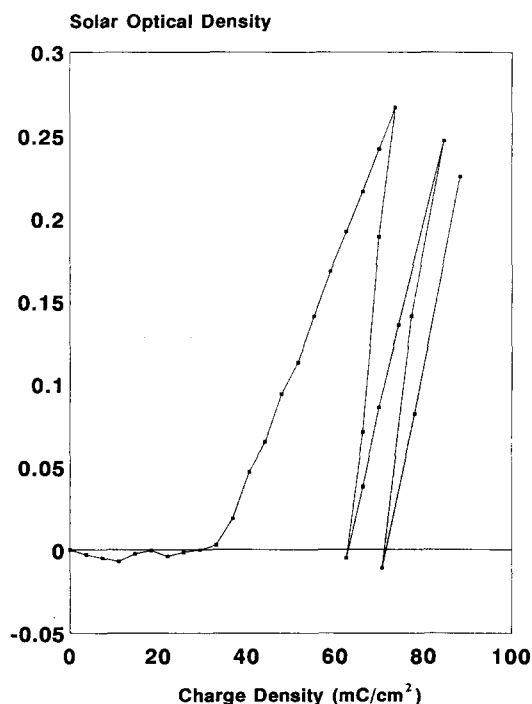


Fig. 3. Solar-weighted OD as a function of charge insertion for d.c.-magnetron sputtered WO₃ (Sputtered from a W-metal target) plotted against inserted charge density to show the effects of cycling the charge in and out. The thickness of the film is approximately 330 nm.

inserted charge density of approximately 60 mC cm^{-2} , indicating that a large amount of charge can be inserted without causing colouration. We see that this is irreversible by the very high potentials (of approximately 6 V *vs.* Li) required to pass further current. The quantity of this irreversibly incorporated charge is very sensitive to the deposition conditions, as can be seen by comparing Figs. 2(a) and 3. As the film is cycled further it is seen that more irreversible charge incorporation occurs, but it is notably less than on the first insertion. We also see that the electrochromic efficiency is increased and tends towards a constant value, leading us to believe that the limit of the irreversible intercalation is being reached as the charge is cycled in and out of the film. In our experience this limit can be quite large (in some cases as large as 100 mC cm^{-2}).

We have checked to see whether lithium is actually being inserted during this initial phase, as there could be some sort of electrolyte degradation or surface reaction occurring that could account for the charge transferred. We inserted approximately 30 mC cm^{-2} into a WO₃ electrode of area 100 cm^2 . The electrode showed no change in optical transmission. The Li_xWO₃ was then dissolved off and the amount of lithium determined by atomic absorption spectroscopy. We recovered

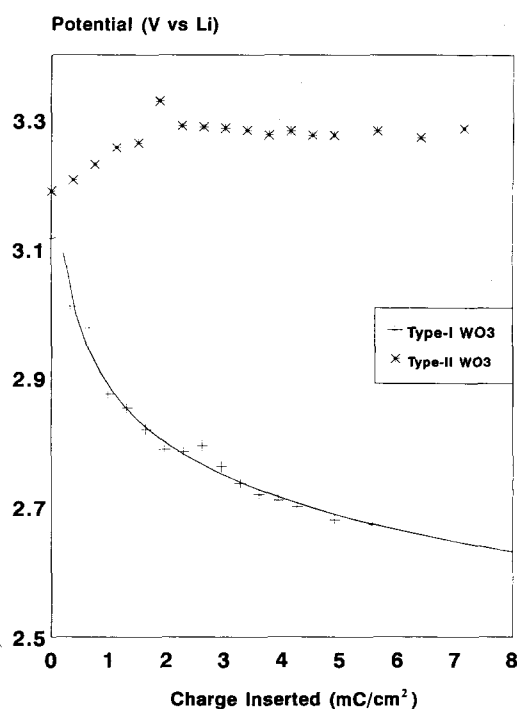


Fig. 4. Results of a coulometric titration of lithium into Groups I and II WO₃, showing radically different behaviour, indicating the two-phase behaviour for the Group II material as described in the text.

69 mg lithium which represents approximately 97% of the charge that was galvanostatically titrated into the WO₃ thin film. This can be compared with <1 mg lithium recovered from an identical control sample which was simply immersed into the electrolyte for the same length of time, undergoing the same cleaning procedure. This proved to us that charge is actually inserted into the WO₃ and not consumed by some side reaction, but does not in any way contribute to the colouring.

The experiments described above indicate that there seems to be at least two states which the lithium can occupy, colouring and non-colouring. To understand this further we show in Fig. 4 results of a coulombmetric titration of lithium into WO₃. We have plotted the open circuit potential V_{oc} versus a lithium-metal RE in a dry LT/PC electrolyte for two different electrodes, examples of Group I and Group II. If a single phase is being formed, V_{oc} of the WO₃ should decrease monotonically as the amount of inserted charge is increased. However, if there are two phases present V_{oc} will remain constant as one phase is gradually transformed into the second phase. From these data, it is clear that we are seeing nucleation of a second phase as lithium is added to the Group II WO₃.

4. Discussion

In this paper we have described the production of thin films of WO₃ which show properties that cannot be described by the normally accepted ideal Beer–Lambert model. We have measured irreversible lithium incorporation that causes absolutely no colouration of the WO₃. This yields an $OD(q')$ characteristic that is radically different to anything reported previously in the literature [9–20]. This effect is a property of the deposition technique, and is also because the majority of the previous measurements were performed on thermally evaporated coatings of WO₃ and not reactively sputtered films. The whole problem of irreversible intercalation is obviously of concern to potential producers of electrochromic devices, because the first choice for large area production will be high growth-rate d.c.-magnetron sputtering, which tends to exacerbate the effect. The initial uptake of charge by the WO₃ will require an undue stress to be placed on the rest of the device during manufacture.

It is difficult to determine what this second phase is, owing to the difficulty of the structural determination of amorphous materials, although it is possible to speculate. An obvious candidate is the water of crystallisation present in the film, which could react with the lithium thus



If this were the case, we would expect to be able to see strong O–H and H–O–H vibrations using FTIR spectroscopy. This was not the case for our sputtered films [22], so we can quite confidently rule out the possibility of a reaction with water.

Another possibility is that there may be excess oxygen in the structure bonded into peroxo-type links, *i.e.* W–O–O–W. This link would be an obviously reactive site. Furthermore, there may be oxygen from the sputtering process trapped within the structure [23]. In this case, if there were any trapped gaseous oxygen it could react something like



It is easily seen that this would produce the two-phase behaviour described above. However, we have no direct evidence from our FTIR work [22] that peroxo-links are formed, and so tend to favour the explanation involving excess oxygen. It is tempting to do this because the sputtering conditions which tend to increase the amount of irreversibly incorporated lithium would also tend to increase the amount of trapped sputtering gases, which in reactive sputtering tends to include a large percentage of oxygen.

5. Conclusions

We have shown that the electrochromic behaviour of WO₃ is very dependent on the thin film deposition conditions. In particular, we have seen that for reactively-sputtered films there can be a large irreversible uptake of lithium. We attribute this to the presence of interstitial gaseous oxygen, which reacts directly with the inserted lithium to form a material that will precipitate out, forming a two-phase compound. Further structural investigations are necessary in order to confirm this hypothesis, and we are currently being undertaken.

This irreversible uptake of lithium will have a deleterious effect on the manufacture of electrochromic devices, because a large amount of charge must be generated before a stable operating condition can be attained.

Acknowledgment

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References

- 1 B. W. Faughnan, R. S. Crandall and P. M. Heyman, *RCA Review*, 36 (1975) 176.
- 2 C. M. Lampert, *Sol. Energy Mater.*, 11 (1984) 1.
- 3 S. F. Cogan, T. D. Plante, R. S. McFadden and R. D. Rauh, *Proc. SPIE Opt. Mat. Technol.*, 823 (1987) 106.
- 4 R. B. Goldner, R. L. Chapman, G. Foley, E. L. Goldner, T. Haas, P. Norton, G. Seward and K. K. Wong, *Sol. Energy Mat.*, 14 (1986) 195.
- 5 S. Passerini, B. Scrosati, A. Gorenstein, A. M. Andersson and G. C. Granqvist, *J. Electrochem. Soc.*, 136 (11) (1989) 3394.
- 6 A. M. Andersson, G. C. Granqvist and J. R. Stevens, *Appl. Optics*, 28 (15) (1989) 3295.
- 7 H. Kaneko, T. Bessho and K. Miyake, *Proc. Electrochem. Soc. Conf. Electrochromic Mat. and Dev.* 1990, p. 288.
- 8 S. F. Cogan, R. D. Rauh, N. M. Nguyen, T. D. Plante and J. D. Westwood, *J. Electrochem. Soc.*, 140 (1993) 112.
- 9 S. K. Mohapatra, *J. Electrochem. Soc.*, 125 (2) (1978) 284.
- 10 K. Yamanaka, H. Oakamoto, H. Kidou and T. Kudo, *Jpn. J. Appl. Phys.*, 25 (9) (1986) 1420.
- 11 K. Fujino, H. Tada and H. Kawahara, *Proc. SPIE Opt. Mat. Technol.*, 823 (1987) 124.
- 12 K. Bange, R. Keller, W. Wagner and F. Rauch, *Proc. SPIE Opt. Mat. Technol.*, 1016 (1988) 50.
- 13 P. V. Ashrit, G. Bader, F. E. Girouard and Vo-Van Truong, *Proc. SPIE Opt. Mat. Technol.* 1149 (1989) 7.
- 14 H. Kaneko, and K. Miyake, *J. Appl. Phys.*, 66 (2) (1989) 845.
- 15 M. G. Hutchins, S. M. Christie and H. Xingfang, *Proc. Appl. Opt. Sol. Energy III, Czechoslovak Nat. Comm. Optics*, 1989, p. 34.
- 16 S. Hashimoto, H. Matsuoka, H. Kagechika, M. Susa and K. S. Goto, *J. Electrochem. Soc.*, 137 (4) (1990) 1300.
- 17 F. G. K. Bauke, J. A. Duffy and R. I. Smith, *Thin Solid Films*, 186 (1990) 47.

- 18 A. Temmink, O. Anderson, K. Bange, H. Hantsche and X. Yu, *Thin Solid Films*, 192 (1990) 211.
- 19 Q. Zhong, S. A. Wessel, B. Heinrich and K. Colbow, *Sol. Energy. Mat.*, 20 (1990) 289.
- 20 S. I. Córdoba de Torresi, A. Gorenstein, R. M. Torresi and M. V. Vázquez, *J. Electroanal. Chem.*, 318 (1991) 131.
- 21 P. W. Atkins, *Physical Chemistry*, Oxford University Press, 1978, Chapt. 18.
- 22 M. S. Burdis, J. R. Siddle and S. Taylor, to be published.
- 23 L. Maissel, in L. Maissel and R. Glang (eds.), *Handbook of Thin Film Technology*, McGraw-Hill, New York, 1970, Chapt. 4.