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Electrochromism in sputter-deposited W–Ti oxide films: Durability enhancement due to Ti

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Abstract

Thin films of W–Ti oxide were prepared by reactive DC magnetron sputtering and were characterized by Rutherford backscattering spectrometry, X-ray diffraction, scanning electron microscopy and atomic force microscopy. The electrochromic properties were studied by cyclic voltammetry in an electrolyte of lithium perchlorate in propylene carbonate and by optical transmittance measurements. The addition of Ti significantly promoted the amorphous nature of the films and stabilized their electrochemical cycling performance and dynamic range for electrochromism.

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1. Introduction

Electrochromic (EC) oxides are mixed conductors for ions and electrons and are able to change their optical properties, persistently and reversibly, between widely separated limits under joint insertion/extraction of ions and electrons [1]. Thin films of these oxides have long been of interest for a variety of uses in optical technology. The largest of these applications is in “smart windows”, whose transmittance of solar energy and visible light can be altered in order to create energy efficiency jointly with a benign indoor environment in buildings [2–4].

Electrochromism was first reported in W oxide [5,6], which remains the most widely studied EC material still today [7,8] and is employed in “smart windows” that are currently introduced by several producers [9–12]. Long-term durability is essential for these windows, and it follows that means to assure this property are of the highest importance. Device durability is contingent on many parameters, and a most significant one is the inherent stability of the W-oxide-based film under extended insertion/extraction of ions.

Durability enhancement of EC films of W oxide was investigated in detail many years ago by Matsuoka and Hashimoto [13–15] who reported on the effect of the incorporation of numerous metallic additives into evaporated films and found that Ti was beneficial and able to extend the cycling durability in a Li^+ -conducting electrolyte by a factor of roughly five. Other, supporting studies on the electrochromism in W–Ti oxide have been reported for films prepared by sputtering [16–19], chemical technology involving spraying [20–22] dipping [16,23] or spinning [24–26], electrodeposition [27,28] and anodization [29]. The enhanced stability has been investigated in depth in recent work on W–Ti oxide films made by sputtering [30,31] and chemical techniques [26]. Data based on electrochemical measurements, transmission electron microscopy, atomic force microscopy and Raman spectroscopy verify [26,30] that the Ti addition makes the crystallization occur at a higher temperature than in a film of pure W oxide. This effect is also advantageous with regard to EC performance [26] since as-sputtered films—prepared at low substrate temperature and high sputter gas pressure as in the present work—have a nanostructure with pores extending across the film thickness [32]. This type of structure allows facile ion intercalation/deintercalation of ions [33] and may be lost upon crystallization and ensuing densification.

This paper reports initial results from a comprehensive study on W–Ti-oxide-based films and highlights the effect of Ti on EC durability. The work is an extension of recent studies on electrochromism in W oxide [34,35] and Ti oxide [36,37].

2. Film preparation and characterization

2.1 Sputter deposition

Thin films of W oxide and W–Ti oxide were prepared by reactive DC magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. Targets were 5-cm-diameter plates of W, W(95 wt.%) + Ti(5 wt.%) and W(90 wt.%) + Ti(10 wt.%) (Plasmaterials), all with 99.99% purity. The sputter system was evacuated to 2×10^{-4} mTorr. Argon and oxygen, both of 99.997% purity, were then introduced through mass-flow controlled gas inlets. The O₂/Ar ratio was set to 0.14, and the pressure was ~30 mTorr. The discharge power P was in the range 200–260 W; unless otherwise noted, the data below were obtained for films prepared at $P = 230$ W. Substrates for optical and electrochemical measurements were unheated 5×5 cm² glass plates coated with transparent and electrically conducting layers of In₂O₃:Sn (denoted ITO) having a resistance of 40 Ω /square. Films for Rutherford backscattering spectrometry were deposited onto carbon plates. The target–substrate separation was 13 cm. Film thicknesses were ~300 nm as determined by surface profilometry using a Bruker DektakXT instrument. Post-deposition annealing of the films, solely for analysis by XRD, was performed by heating them in air at 400 °C for 1 h by use of a conventional tube furnace.

2.2 Compositional characterization

Elemental characterization of the films was performed with Rutherford backscattering spectrometry (RBS) using 2 MeV ⁴He ions backscattered at an angle of 170°. The RBS data were fitted to a model of the film–substrate system by use of the SIMNRA simulation program [38]. Characterizing the films as W_{1-x}Ti_xO_y, we found (x , y) to be (0.12 $\pm$ 0.06, 2.96 $\pm$ 0.10) for deposition from the target with 5 wt.% Ti and (0.20 $\pm$ 0.06, 2.84 $\pm$ 0.10) for the target with 10 wt.% Ti, respectively; we refer to these film compositions simply as W_{0.88}Ti_{0.12}O₃ and W_{0.8}Ti_{0.2}O₃ below. It should be noted that

the oxygen contents are consistent with the preservation of local chemical bonds both for W and Ti oxide.

Film densities were evaluated from surface profilometry and RBS data, as described elsewhere [34], and were found to be $\sim 6.0 \text{ g/cm}^3$. In our earlier work [34], we found the density of W oxide films to be 5.2 g/cm^3 , i.e., somewhat smaller than here.

2.3 Structural and morphological characterization

Structural characterization of as-deposited and annealed films was performed with X-ray diffraction (XRD) using a Siemens D5000 instrument working with $\text{CuK}\alpha$ radiation. Fig. 1 reports characteristic data for films of W oxide and $\text{W}_{0.8}\text{Ti}_{0.2}\text{O}_3$ in as-deposited state and after annealing. The as-deposited samples showed nothing but diffraction features due to ITO (in agreement with JCPDS–ICDD card number 88-0773) and hence were amorphous. The two types of films clearly perform very differently under heat treatment; the pure W oxide film crystallizes into a well characterized monoclinic structure (JCPDS–ICDD card number 83-0950), whereas the W–Ti oxide films remain amorphous. Analogous results were found for films deposited with other discharge powers in the sputter plasma. This crystallization-impeding effect of Ti is consistent with previous findings, as mentioned in the Introduction.

Fig. 1. X-ray diffractograms for films of the shown compositions and studied in as-deposited state and after annealing at 400 °C. The (hkl) indices correspond to the monoclinic phase of WO_3 . Arrows indicate diffraction peaks due to ITO. Note that the vertical scales are different for the two sets of data.

Surface structures of as-deposited films of WO_3 , $\text{W}_{0.88}\text{Ti}_{0.12}\text{O}_3$ and $\text{W}_{0.8}\text{Ti}_{0.2}\text{O}_3$ were investigated by scanning electron microscopy (SEM) using a Zeiss 1550 FEG Gemini instrument with an acceleration voltage of 10 kV. Fig. 2 shows SEM micrographs of the surface morphologies as recorded at a magnification of 300,000 $\times$. Nanofeatures can be seen on the scale of 5–10 nm as well as an apparent “crack pattern” with a linear extent of 50–100 nm. Importantly, no evidence was found for any relationship between surface nanostructure and Ti content.

Fig. 2. SEM micrographs of sputter-deposited oxide films with the shown compositions. Scale bars define the magnification.

Additional information on surface nanotopography was acquired through atomic force microscopy (AFM) employing a PSIA XE150 SPM/AFM instrument having an etched cantilever with a tip radius of 10 nm and 35° apex angle. Data were taken with a constant force of $\sim 10^{-7}$ N, scans were made for areas of 1000×1000 nm, and root-mean-square roughness R_{rms} was evaluated over this area. Fig. 3 shows an AFM micrograph for a film of $\text{W}_{0.88}\text{Ti}_{0.12}\text{O}_3$ and shows nanofeatures with in-plane extents of 50–100 nm and heights of a few nm. Films of WO_3 and $\text{W}_{0.8}\text{Ti}_{0.2}\text{O}_3$ displayed similar AFM data. Values of R_{rms} were ~ 2 nm for each of the films. AFM and SEM data are consistent, but detailed comparisons are not meaningful.

Fig. 3. AFM micrographs of a sputter-deposited oxide films with the shown composition.

3. Electrochemical and optical data

3.1 Cyclic voltammetry

Cyclic voltammetry (CV) measurements were performed using a Solartron 1286 Electrochemical Interface in a three-electrode electrochemical cell. The electrolyte was 1 M LiClO_4 in propylene carbonate (Li-PC), and lithium foils served as reference and counter electrodes. All measurements were performed inside a glove box with inert argon atmosphere. The voltage sweep rate was 10 mV/s.

Fig. 4 shows CV data for films of pure W oxide in the voltage ranges 2.0–4.0 and 1.7–4.0 vs. Li. Clearly the specific range is important, and rapid degradation takes place

during 80 CV cycles for the larger voltage interval whereas relative stability is found for the smaller range (which was used in earlier studies of EC films of W oxide [34,35]). We chose the larger voltage range below in order to highlight the effects of Ti additions.

Fig. 4. Cyclic voltammograms for pure W oxide films immersed in 1 M Li-PC. Data were taken after the indicated numbers of cycles and for voltage sweep ranges being 2.0–4.0 V vs. Li (panel a) and 1.7–4.0 V vs. Li (panel b).

Fig. 5 reports cyclic voltammograms for films of $W_{0.88}Ti_{0.12}O_3$ and $W_{0.8}Ti_{0.2}O_3$ in a way that allows direct comparison with corresponding data for the pure W oxide film in Fig. 4(b). It is evident that the addition of Ti prevents degradation and that this effect is strongest at the largest Ti content. The discharge power in the sputter plasma plays some role too, as we elaborate below.

Fig. 5. Cyclic voltammograms for W–Ti oxide films of the shown compositions immersed in 1 M Li–PC. Data were taken after the indicated numbers of cycles and for the voltage sweep range 1.7–4.0 V vs. Li.

The evolution of the inserted and extracted charge density Q , as a function of the number of voltammetric cycles was extracted from our CV data and is illustrated in Fig. 6(a) for the pure W oxide film. It is again apparent that the W oxide film loses its charge capacity rapidly, and the film displays only weak electrochemical activity after 80 cycles. It is also interesting to consider the electrochemical irreversibility, i.e., the difference between inserted and extracted charge densities for successive voltammetric cycles $\delta Q = |Q_{\text{Inserted}} + Q_{\text{Extracted}}|$. As reported in Fig. 6(b), there is significant irreversibility during the first cycles, possibly as a consequence of irreversible Li incorporation [39]. The film displays large irreversibility particularly for cycle numbers around 50. For the Ti-containing films, on the other hand, the decline of the charge density is much slower, as is readily seen in Figs. 7(a) and (c). Quasi-equilibrium between inserted and extracted charge density prevails for the Ti-conducting samples after some initial voltammetric cycling. It is interesting to note that the lowest sputter power yielded the highest electrochemical stability.

Fig. 6. Inserted and extracted charge density for pure W oxide films during voltammetric cycling Q (panel a) and difference in charge density for successive charge insertions and extractions δQ (panel b), as obtained from data shown in Fig. 4(b). Symbols denoting data were joined by straight lines.

Fig. 7. Inserted and extracted charge density during voltammetric cycling Q and difference in charge density for successive charge insertion and extraction δQ for $W_{0.88}Ti_{0.12}O_3$ [(panels (a) and (b)] and $W_{0.8}Ti_{0.2}O_3$ [(panels (c) and (d))] films. The films were sputter deposited at the stated values of discharge power in the plasma. Symbols denoting data were joined by straight lines.

4. Optical transmittance

Optical transmittance was recorded in two ways: Monochromatic transmittance T was determined at the mid-luminous wavelength $\lambda = 550$ nm in situ during CV cycling using an Ocean Optics fiber-optic instrument, and spectral transmittance was determined in the $300 < \lambda < 2500$ nm interval on films removed from the glove box by use of a Perkin–Elmer Lambda 900 spectrophotometer.

Fig. 8 shows $T(\lambda)$ for films of pure W oxide and of $W_{0.88}Ti_{0.12}O_3$ and $W_{0.8}Ti_{0.2}O_3$ in fully bleached and colored states after 20 CV cycles between 1.7 and 4.0 V vs. Li. The spectral data are rather similar and show evidence of optical interference, especially for films in their bleached states. However, clear differences in the optical data evolved as the cycling progressed, which is apparent from Fig. 9 illustrating maximum and minimum monochromatic transmittance at $\lambda = 550$ nm, denoted T_{bl} and T_{col} , respectively. It is apparent that electrochromism is rapidly lost for the W oxide film whereas it persists to a much higher degree for the Ti-containing films. The film of pure W oxide attained a brownish-yellowish color upon extended CV cycling, which is consistent with Li accumulation.

Fig. 8. Spectral transmittance for films with the shown compositions after 20 voltammetric cycles in 1 M Li–PC. Data are shown for the fully bleached and colored states.

Fig. 9. Evolution of maximum and minimum transmittance at the wavelength 550 nm for films of the shown compositions immersed in 1 M Li-PC. Data were taken after the indicated numbers of cycles and for the voltage sweep range 1.7–4.0 V vs. Li. Symbols denoting data were joined by straight lines.

We also extracted the coloration efficiency (CE) for the various films. This quantity is defined as $\ln(T_{bl}/T_{col})/\Delta Q$, where ΔQ is the inserted charge density accompanying the transmittance change. The expression disregards minor reflectance differences between the bleached and colored states. Clearly the CE should be as large as possible for EC devices.

Fig. 10 shows data on CE at $\lambda = 550$ nm for the samples reported on in Fig. 9, and also for similar films prepared at different magnitudes of the power in the discharge plasma. Expectedly, the CEs are somewhat larger than those for W oxide films investigated at 2.0 and 4.0 V vs. Li in earlier work [34]. Data for different values of P indicate that a small power tends to give a low magnitude of the CE. Hence there also seems to be a correlation between low CE and high electrochemical stability. The increased CEs for W oxide films cycled more than 50 times is spurious and signals sample degradation, as apparent from Fig. 9.

Fig. 10. Evolution of coloration efficiency at the wavelength 550 nm for W oxide and W–Ti oxide films of the shown compositions immersed in 1 M Li–PC. The films were sputter deposited at the stated values of discharge power in the plasma. Data were taken after the indicated numbers of cycles and for the voltage sweep range 1.7–4.0 V vs. Li. Symbols denoting data were joined by straight lines.

5. Remarks and conclusions

We presented results from an investigation of the role of Ti additions to sputter deposited electrochromic W oxide films. The pure W oxide film degraded rapidly in Li–PC upon cycling in the range 1.7–4.0 V vs. Li, which may be associated with chemical reactions between Li and interstitial oxygen incorporated as a consequence of the sputtering process [39], although influence from the disintegration of the transparent conductor of ITO is another possibility [40]. The Ti was found to promote stability both for crystallization at elevated temperature and for the electrochromic performance under extended cycling in a Li-conducting electrolyte. Our data are consistent with those in prior work [14–18,26,30] as regards crystallization and support earlier evidence concerning the ability of Ti to prevent permanent incorporation of Li. Furthermore, our data indicate that low sputtering powers are connected with improved stability under electrochemical cycling. More generally, our work points at possibilities to extend the performance and/or durability of electrochromic devices, such as smart windows.

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