Characterization of tungsten–titanium oxide electrode for electrochromic applications

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1. Introduction

Tungsten oxide is an opto-electronic material and can be used as windows in solar cells, in electrochromic (EC) devices, in information displays and in color memory devices [1–5]. Numerous physical, chemical and solid-state methods for synthesizing tungsten oxide films have been described [1–13]. Sangaletti et al. [8], using W–Ti alloy targets and radio-frequency (RF) sputtering, fabricated an amorphous W–Ti–O layer and analyzed the film morphology and structure. Wang and Hu [12] prepared TiO$_2$-doped WO$_3$ films via the peroxo sol–gel route and discussed the effect of adding Ti. Yamamoto et al. [4] synthesized WO$_3$ films using an RF sputtering system and explored the effect of the oxygen flow rate. Karuppasamy and Subrahmanyam [14] investigated the effect of oxygen chamber pressure on the EC properties of titanium-doped tungsten oxide thin films using co-sputtering metallic titanium and tungsten. Sputtering is a widely used technique for preparing thin films, and is superior in terms of composition reproducibility and thinness on a large-area substrate. Co-sputtering can be performed with a range of values of relevant variables to find the conditions that optimize EC behavior. This study is a preliminary survey based on co-sputtering with varying ion beam power. The relationships between electrochromic applications and the other variables, such as gas flow rate, bias voltage and deposition time, are investigated. The goal is to gain insights that can be exploited on an industrial scale to optimize fabrication conditions.

2. Experimental details

Indium tin oxide (ITO)-coated glass, with a sheet resistance of 10 $\Omega$ cm and dimensions of 2 cm $\times$ 2 cm was selected as a substrate. Two targets, tungsten and titanium, were co-sputtered using a pulsed sputtering deposition system. Table 1 presents the experimental deposition parameters. Specimen assemblies were deposited at ion beam powers of 100, 200, 300, 400 and 500 W, and denoted S1, S2, S3, S4 and S5, respectively, for convenience. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)
were used to elucidate microstructural changes. The morphology and cross-sectional microstructures of the specimen assemblies were examined by field emission scanning electron microscopy (FESEM). The surface topography of the specimen assemblies was examined by atomic force microscopy (AFM), which measures the root mean square roughness ($R_{\text{rms}}$) in a square area of 3 μm. The same vertical scale was chosen for all the specimens for comparison.

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**Fig. 1.** XRD patterns revealing that the crystalline structure is formed gradually as the ion beam power increases.

**Fig. 2.** XPS spectrum of the specimen assemblies.

**Fig. 3.** SEM images of the microstructure at different implanted powers, indicating that the films consisted of nanograins; the morphology became gradually coarser from S1 to S5.
EC experiments were performed in a three-electrode cell. The specimen assemblies were cycled in a non-aqueous electrolyte (0.1 M LiClO₄ in propylene carbonate, PC). A highly pure graphite, a saturated calomel electrode (SCE) and specimen assemblies were used as the counter electrode, the reference electrode and the working electrode, respectively. Transmittance spectra were obtained at constant potential (±1.0 V). The transmittances (ΔT, %) of the specimen was plotted between bleached and colored states (λ = 550 and 800 nm).

3. Results and discussion

Fig. 1 shows the XRD patterns of the specimen assemblies. Except for S5 (power 500 W), the films (S1–S4 assembly) have amorphous characteristics. The peaks of this spectrum (S2–S5 assembly) became more intense and narrow than those of the corresponding film deposited at 100 W. At a power of 500 W, phases {1 1 0}, {1 0 2}, {1 1 2}, {2 0 2}, {1 0 4}, {2 2 2} are present in

Fig. 4. Cross-sectional SEM micrographs at different ion beam powers.

Fig. 5. Variation of thickness with ion beam powers; a steady state exists at 300 W.
WO₃ (1 0 4) for Ti₂O₃ and (1 1 1) for Tiₓ₇₋ₓWₓO₂ₓ. Increasing the ion beam power requires a higher ion beam energy, given other fixed process parameters. Such the high energy may be responsible for the existence of a crystalline structure. Fig. 2 shows the XPS survey spectra of the specimen assemblies. The figure presents tungsten, titanium and oxygen peaks, and reveals a trace amount of surface physisorbed carbon with no other surface impurity on the surface of the film.

The surface morphology characterization by SEM indicates that the specimen assemblies consisted of nanograins in Fig. 3. Its microstructure is fine and dense. The surface grains are quite homogeneous and uniform in size and distribution, because the
energetic ion bombardment during the fabrication process remixes the surface atoms and clusters. Rice-shape pellets were observed gradually from S1 to S5, and are responsible for the coarse morphology.

Fig. 4 shows the cross-sectional SEM micrographs of the specimen assembly films prepared at varying power. A columnar structure was found. Fig. 5 plots the film thickness versus ion beam power. When the ion beam power is low, fewer energetic atoms are sputtered from the targets. Therefore, when the deposition rate is low, the film is thin. The thickness of the film increases with the ion beam power. However, the slope of the curve at an ion beam power of less than 300 W is greater than that of the curve obtained at powers of 400 and 500 W, and indicates a steady state. The thickness of the film reaches a maximum of around 1800 nm at 500 W (Fig. 5). Re-sputtering causes the input kinetic energy and momentum to be so high that the deposited material is again vaporized by sputtering, reducing the growth velocity and the final thickness of the film [15,16]. The steady state of growth exists when the ion impingement rate equals the sputtering rate.

Fig. 6 shows AFM images of 3 μm x 3 μm scan areas for all specimens. The top-view image presents surface morphology with a roughness of between 1.3 and 3.9 nm, as listed in Table 2. Higher ion beam power yields a coarser morphology. This finding is consistent with the plane-view SEM image. The films exhibited no apparent cracking.

Fig. 7 plots the transmittances (ΔT (%)) of the specimen assembly films between bleached and colored states curves (λ = 550 and 800 nm). The maximum ΔT (%) for 550 nm is 55% and for 800 nm is 40%. The value of ΔT (%) is maximum in both cases at 200 W. It decreases when the ion beam power is either too low or too high.

WO₃ film in a bleach state (transparent) can be switched reversibly into a colored state (dark blue) by the insertion of both WO₃, according to the reaction:

\[
\text{WO}_3 + x\text{M}^{+} + x\text{e}^- \rightarrow \text{M}_x\text{WO}_3
\]

where M⁺ is H⁺, Li⁺, Na⁺ or K⁺ ions. The above equation describes a reduction reaction, which results in coloration, and an oxidation reaction, which results in transparency. The reaction rate depends on the concentration of ions, oxygen deficiency, temperature and other variables.

In EC experiments, the transport of Li-ions is a major factor that affects EC behavior. The mobility of Li in the films depends strongly on the microstructure, including the density of the film, its degree of porosity and other factors [17,18]. The films, as revealed by SEM, are composed of nanograins and the coarseness of the morphology increased with the ion beam power. The coarse morphology suits the transport of Li ions and improves EC behavior [19].

When Eq. (1) is reversible, EC behavior is improved. An irreversible crystalline phase is not appropriate for EC applications [20]. High ion beam power produces a crystalline structure, as revealed by XRD, which fact may explain the poor EC behavior. The transport of Li ions and the reversibility of Eq. (1) also were responsible for good EC behavior.

Increasing the ion beam power, as discussed above, promoted the transport of Li ions and made the reaction irreversible. Varying ion beam power to improve EC behavior involves a trade-off with reducing EC behavior. In this study, EC behavior is favorable when the device is operated at the optimal ion beam power of 200 W.

4. Conclusions

The substrate, a conductive glass being coated ITO thin films, was deposited by pulsed co-sputtering deposition system. The above analytical results support the following conclusions:

(1) The peaks of this spectrum became more intense and narrow as the ion beam power increased.
(2) The film surface grains are quite homogeneous and uniform in size and distribution. A higher ion beam power yields a coarser morphology.
(3) The thickness of the film increases with the power of the ion beam. The slope of the curve at an ion beam power of less than 300 W is greater than that of the curve obtained at a power of 400 or 500 W.
(4) The maximum ΔT (%) at 550 nm is 55% and at 800 nm is 40%. In both cases, ΔT (%) is maximal at 200 W. ΔT (%) decreases when the ion beam power is either too low or too high.

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