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The colored and bleached properties of tungsten oxide electrochromic films with different substrate conductivities

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Abstract

Tungsten oxide films have been deposited by reactive RF magnetron sputtering. The electrochromic properties were characterized by cyclic voltammetry and UV–visible spectrometry. The oxide films were deposited on substrates with different electrical conductivities. The sheet resistances of the ITO electrodes used in this study were 10, 50 and180 Ω/cm^2, respectively. Experimental results demonstrate that the electrical conductivity of the electrode material strongly influences the response time of the WO_3 electrochromic film, which is explained by the different numbers of lithium ions transported at the different electrode conductivities. The ITO material with 10 Ω/cm^2 gave the best response time of the WO_3 electrochromic films.

Keywords: Tungsten oxide; Electrochromic; Thin films; Sputtering

1. Introduction

In recent years, electrochromic materials have been widely studied and applied because their optical transmittance can be adjusted [1–5]. Thus, smart windows that can automatically respond to outdoor light can be synthesized. Electrochromic devices have many applications such as smart windows, optical shutters, rear-view mirrors, pattern display devices, etc. [6]. We chose tungsten oxide (WO_3) as the electrochromic material in this study because of its excellent coloration efficiency compared with other materials. The generally accepted electrochromic process for a WO_3 film to adopt the colored/bleached state, which is reversibly achievable by injection of electrons and ions, can be summarized by the following equation:

$$WO_3 + xM^+ + xe^- \leftrightarrow M_xWO_3 \quad (1)$$

where M^+ is H^+, Li^+, Na^+ or K^+. WO_3 films can be prepared by a variety of methods, including electron-beam evaporation, sputter deposition, thermal evaporation, chemical vapor deposition, and the sol–gel process [7–13]. Among these methods reactive sputtering is the most suitable for large area applications such as automobile glass and architecture building glass [14,15].

The purpose of this paper is to investigate the effect of substrate conductivity on the electrochromic capability of WO_3 films and to identify the most suitable electrode conductivity from its performance.

2. Experimental

2.1. Process preparation

The WO_3 films were prepared by RF magnetron reactive sputtering. The substrates used to receive the deposited WO_3 films were indium-tin oxide (ITO) electrodes with sheet resistances of 10, 50 or 180 Ω/cm^2. The area of the samples was about 2.6 cm × 2.5 cm. The sputtering was conducted from a 3-in. diameter tungsten target (99.9% purity) in an atmosphere containing argon and oxygen gas mixtures. The distance between the substrate holder and target was approximately 16 cm. The base pressure was 3.0×10^{-6} Torr or better and the working pressure was 5.0×10^{-3} Torr. The RF sputtering power used was 100 W for all the deposition processes. The thicknesses of deposited films in all cases were controlled to about 300 nm.

2.2. Characterization

The structures of the deposited films were studied by X-ray diffraction (XRD) with monochromatic Cu Kα as a radiation source at 30 kV and 20 mA.

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Cyclic voltammetry (CV) was performed to characterize the electrochromic behavior of the films, using a potentiostat system with a standard three-electrode configuration consisting of the sample as the working electrode, a conventional saturated calomel electrode (SCE) and a carbon rod counter electrode. The measurements were carried out in 1 M $LiClO_4$/propylene carbonate (PC) using an EG&G Model-263 potentiostat. The optical transmittance measurements were performed in the optical region from 300 to 800 nm with a UV spectrophotometer.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of a typical WO_3 film deposited on ITO/glass. It can be seen that the as-deposited film is amorphous. Normally, amorphous WO_3 films are more suitable than crystalline WO_3 films for electrochromic applications. A crystallized structure is less favorable for ions to diffuse through because of the densely packed atomic structure, because the lithium ion movement through the film is obstructed by the dense structure leading to a lower response time.

The transmittance variation for the film reflects the production and decline of the color centers during intercalation/extraction of considerable numbers of Li^+ and e^-. Fig. 2 shows the transmittance spectra of the films in the bleached and colored states in the range between 300 and 800 nm. The transmittances at 550 nm in the bleached states were about 79, 91 and 85% for the films deposited on substrates with sheet resistance of 10, 50 and 180 Ω/cm^2, respectively. The highest change in transmittance of about 91% between the bleached and colored states was obtained on the WO_3 film deposited on the substrate with 50 Ω/cm^2 sheet resistance. The higher transmittance illustrates the better coloration efficiency for the film with 50 Ω/cm^2 sheet resistance.

Fig. 3 shows that the switching response time was 15, 65 and 100 s with the ITO substrate's sheet resistance at 10, 50 and 180 Ω/cm^2, respectively. The maximum current value occurs as the sheet resistance of the substrate decreases, due to conductive electrons increasing with decreasing sheet resistance of the substrate. It indicates that the sheet resistance value of the substrate has a great effect on the speed of Li ion intercalation/extraction between the films and the response time as well.

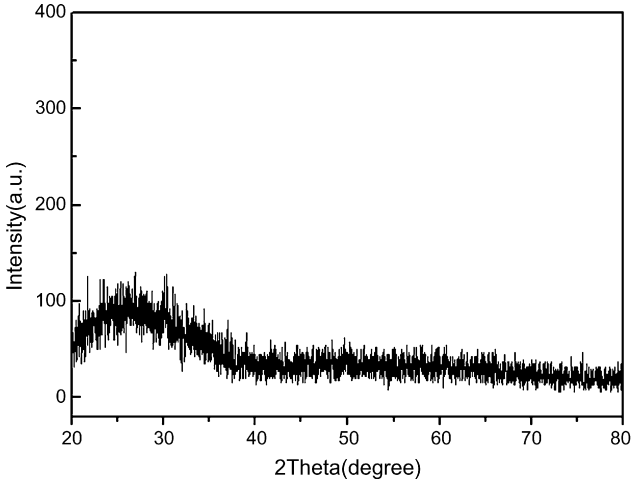

Fig. 1. XRD pattern of a typical as-deposition WO_3 film.

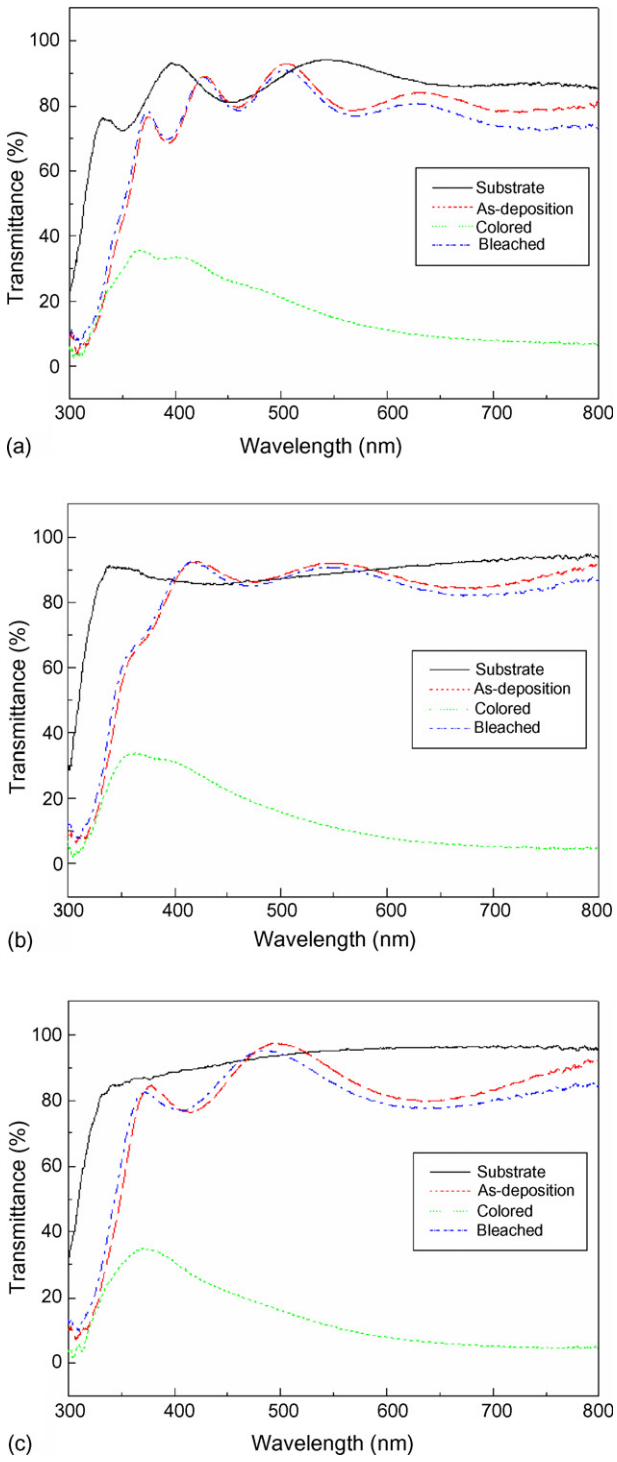

Fig. 2. Transmittance spectra of the WO_3 films using different sheet resistance substrates (a) 10 Ω/cm^2; (b) 50 Ω/cm^2; (c) 180 Ω/cm^2, in the range 300 and 800 nm.

The successive cycles are observed to form almost a single curve for many bleached/colored cycles after the initial stabilization and optimization cycle. Fig. 4 shows the cyclic voltammogram patterns of WO_3 films on substrates of different sheet resistance. Voltages between −1.0 and +1.0 V relative to SCE were applied with a scan rate of 10 mV/s. The current arises from application of a cathodic potential from +1.0