

Electrochromic Device with Functions of Rapid Switching Duty Cycle and Infrared Suppression

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Abstract

In this paper, the electrochromic device with functions of rapid duty cycle and infrared (IR) suppression. The electrochromic device is simultaneously not only having high optical modulation but also IR-suppression by using the multilayered AZO/Ag/AZO structure. The AZO/Ag/AZO structure is using to be transparent electrode and the nano-crystalline WO₃ is using to be electrochromic layer. The electrochromic device showed an optical modulation (ΔT) at a wavelength of 550 nm was 74.8 %, which is the difference between the transmittance of the colored state (14.61 %) and that of the bleached state (89.36 %). The response time of the device is found to be about 11.9 s for colored state and 6.8 s for bleached state.

Keywords: Electrochromic Device, AZO/Ag/AZO transparent electrodes, Tungsten oxide, Nano-crystalline, Smart window

Introduction

Recently, the electrochromic materials have been widely studied [1-3]. The transition metal oxides materials such as WO₃, V₂O₅, MoO₃, NiO_x, and SnO₂ have been proposed to be promising electrode materials for electrochromic devices. [4-6]

Tungsten oxide (WO₃) is the appropriate electrochromic material because its characteristic of multiple valence states, high coloration efficiency and good stability compared with other materials. The optical variation of the WO₃ film can be controlled by a reversible applied voltage with the intercalation/extraction of cations (such as H⁺, Li⁺ or Na⁺) and electrons. Several studies are using different deposition methods for preparing the WO₃ thin films such as sputtering, pulsed laser deposition, electron beam evaporation, chemical vapor deposition and hydrothermal method [7-11].

Recently, there are few studies showing the AZO/Ag/AZO structure to be transparent electrode in the electrochromic devices [你的 EDL]. It is necessary to investigate the electrochromic properties of the WO₃ film on the AZO/Ag/AZO films in electrochromic devices to achieve energy efficiency and user comfort in the built environment.

In this paper, the proposed electrochromic device obtained the optical modulation (ΔT) of 74.8 % at 550 nm wavelength, the response time were obtained about 11.9 s (for colored state) and 6.8 s (for bleached state). So far, we were the first team in the world successfully to make the electrochromic devices of two functions. The two functions are Low-E glass (for bleached

state) and electrochromic devices (for colored state). These results show the AZO/Ag/AZO thin films to be a good candidate for high quality electrodes scheme in electrochromic devices applications.

Experimental Methods

A. AZO/Ag/AZO Transparent Conducting Oxide Films

The AZO/Ag/AZO multilayer films were deposited on the glass substrate (Corning Eagle XG ; 70 × 50 × 0.5 mm³) by rf magnetron sputtering using an AZO ceramic target (99.9995% purity, 200 mm diameter, 50 mm thickness Al₂O₃ : ZnO = 2 : 98 wt %) and electron beam evaporation using a Ag chips (99.999% purity). The AZO thin film sputtering was performed in an Ar (180 sccm) atmosphere at a pressure as high as 2.4 Pa (base pressure 4.0×10⁻⁴ Pa) with a deposition rate of 0.028 nm s⁻¹ at the RF power of 250W. The substrate temperature kept at 70 °C and the distance between substrate and target was 15 cm.

The electron beam chamber was pumped down to 0.35 Pa prior to deposition. The variation of substrate temperature during deposition was maintained within ±5 °C. Substrate temperature was controlled in the range of 30 – 100°C and the deposition rate at 0.01 nm/s⁻¹. Deposition of Ag layer was performed in the evaporation chamber with 6 kV and 20 mA. The thickness of the AZO layer was 30 nm and the Ag was 8 nm for this study, as referenced in [12]. Finally, the AZO/Ag/AZO multilayer transparent electrode was annealed in the vacuum atmosphere at 400 °C, that's due to further enhance the optoelectrical properties of AZO/Ag/AZO multilayer films.

B. WO₃ Electrochromic Films

The WO₃ films were deposited on the AZO/Ag/AZO films by rf magnetron sputtering using a WO₃ ceramic target (99.9% purity, 200 mm diameter, 50 mm thickness) in an Ar (100 sccm) + O₂ (40 sccm) atmosphere at a pressure as high as 0.667 Pa (base pressure 4.0×10⁻⁴ Pa) with a deposition rate of 0.027 nms-1 at the RF power of 300W. The substrate temperature kept at 27 °C and the distance between substrate and target was 15 cm. The thickness of WO₃ film was controlled at 300 nm.

C. Characterization Techniques

Transmittance-modulation measurements were performed with an electrolyte solution of 1 M lithium perchlorate (LiClO₄, 99%, Alfa Aesar, UK) in propylene carbonate (PC, 99%, Alfa Aesar, UK) using a UV-vis spectrophotometer (JASCO V670, Japan) and a potentiostat (VersaStat II Potentiostat/Galvanostat, Princeton Applied Research, USA). The cyclic voltammetry measurement employed the WO₃ films, Ag/AgCl electrode,

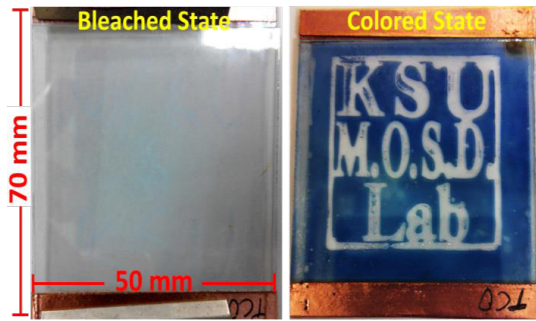


Fig. 1 The photograph of the electrochromic device (70 × 50 mm) at (a) colored and (b) bleached states.

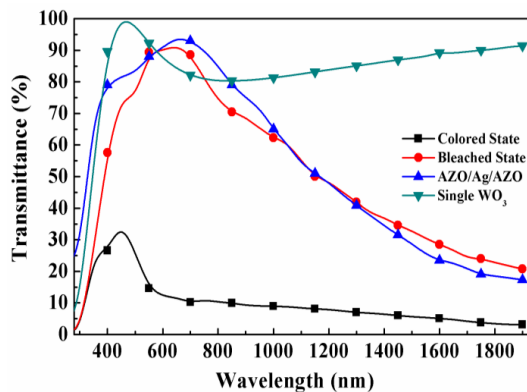


Fig. 2 Optical transmittance spectra under the bleached and colored state of the device at the wavelength of 200 to 1900 nm.

and Pt sheet as the working electrode, reference electrode, and counter electrode, respectively. The coloration and bleaching potential were kept constant at +2.0 V and -2.0 V, respectively. The cross-sectional view was analyzed using transmission electron microscopy (field emission gun (FEG)-TEM, FEI TECNAI G2 F20) (FEI/ USA /Hillsboro) operating at 200 kV.

Results and Discussion

Fig. 1 shows the photograph of the electrochromic device (70 × 50 mm) switched at colored and bleached states. When the applied voltage operated at -2V, the color is changing from transparency to deep blue (colored state). When the applied voltage operated at 2V, the color is changing from deep blue to transparency (bleached state). In the mechanism of color changing, this is due to the Li^+ ions intercalated into and deintercalated out of the WO_3 layer in the proposed device. The electrochromic device reveals a good contrast ratio of 74.8 % between colored and bleached states.

Fig. 2 shows the optical transmittance spectra under the bleached and colored state of the device at the wavelength of 200 to 1900 nm. The transmittance of the AZO/Ag/AZO films shows the value of 86.33% at the wavelength of 550 nm. The as-deposited WO_3 film shows the transmittance of about 92.26 % at a wavelength of 550 nm. The transmittance of the WO_3 films can achieve to 14.61 % at colored state and

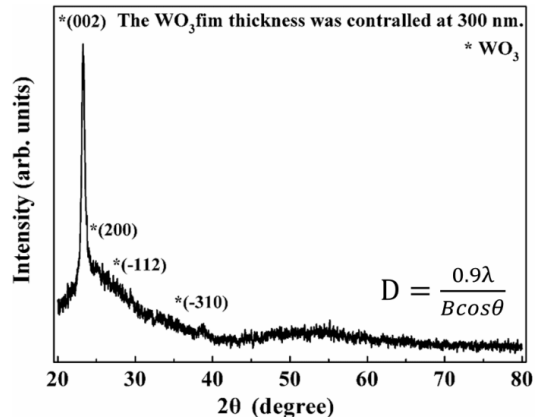


Fig. 3 The full width at half maximum (FWHM) of XRD (002) peaks and the average crystallite size corresponding to the WO_3 thin film.

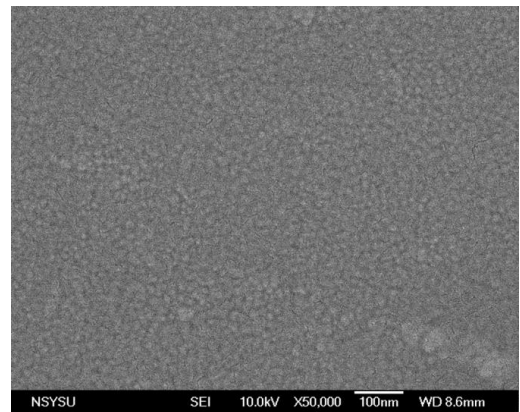


Fig. 4 Field-emission scanning electron microscope images of the WO_3 thin films. (The thickness of WO_3 film is fixed at 300 nm)

achieving to 89.36 % at bleached state under the wavelength of 550 nm. It noted that the ΔT (%) = T (bleached, 550 nm) – T (colored, 550 nm) = 74.8 %. We found that the infrared transmittance can be suppressed no matter operating at bleached or colored state. Because the reflection by Ag layer in infrared region causes the transmittance decreased. The low near-infrared transmittance is very suitable for low emissive (Low-E) glass in green building techniques [13-15]. Therefore, the proposed device operating at bleached state could be a potential application to low-E glass.

Fig. 3 shows the full width at half maximum (FWHM) of XRD (002) peaks and the average crystallite size corresponding to the WO_3 thin film. The crystallite size can be calculated by using the Scherrer's equation as follows [16]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where $\lambda = 1.54 \text{ \AA}$ and $\beta = B - b$ (B is the observed FWHM and b is the instrument function determined from the broadening of the monocrystalline silicon diffraction line). An X-ray diffraction analysis revealed that the WO_3 film shows the average crystallite size and full width at half maximum

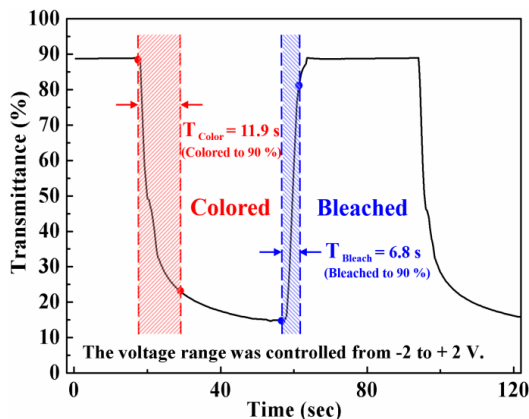


Fig. 5 The transmittance at wavelength of 550 nm of the electrochromic device under voltage of ± 2 V versus state of color and bleach.

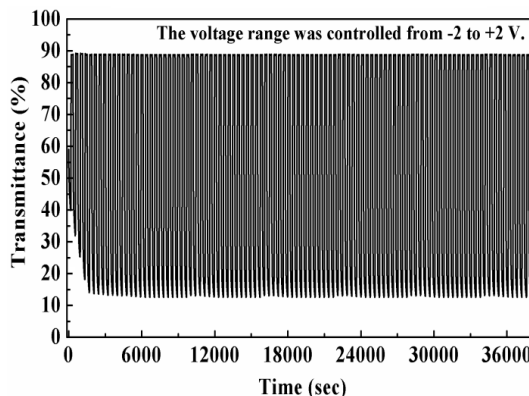


Fig. 6 Continuous potential cycling curves up to 100 cycles for WO_3 films.

(FWHM) are around 14.65 nm and 0.59° , therefore, the WO_3 film shows the nano-crystalline structure. For the traditional electrochromic device glass, the WO_3 film (polycrystalline) is less favorable for ions to diffuse through, that because the lithium ion movement through the film is obstructed by the dense structure leading to a slower response time. The nanostructure WO_3 films can make a short diffusion path for ion-tungsten oxide interaction that can reduce the response time [17-18].

Fig. 4 shows the field-emission scanning electron microscope (FE-SEM) images of the WO_3 thin films. It can be found that the grain size of the WO_3 film is less than 15 nm on the surface morphologies. Therefore, we defined the crystal structure of the WO_3 thin film is microcrystalline structure. The fabricated device achieved a rapid response time, adequate optical modulation depth, high stability, and a long electrochromic device lifetime.

Fig. 5 shows the transmittance at wavelength of 550 nm of the electrochromic device under voltage of ± 2 V versus state of color and bleach. The costing time of coloration and bleaching (T_{color} and T_{bleach}) are defined as the required time for

Table 1. Comparison of electrochromic properties between the previous literatures and the proposed electrochromic device

Ref.	Process Method	WO_3 Thickness (nm)	Transparent Electrode	Area (cm^2)	Coloration Times (sec)	Bleaching Times (sec)	Optical Modulation ΔT (%)
[24]	RF magnetron sputtering	300	ITO	6.5	15	X	65
[27]	DC magnetron sputtering	621	ITO	X	32	8	75
[28]	DC magnetron sputtering	X	ITO	25.0	10	20	55
[29]	DC magnetron sputtering	350	ITO	2.5	18.6	10	40
[30]	DC magnetron sputtering	300	ITO	9.0	X	X	57
[31]	DC magnetron sputtering	300	ITO	5.0	X	X	56.7
[32]	DC magnetron sputtering	270	AZO	4.0	X	X	50
This study	RF magnetron sputtering	300	AZO/Ag/AZO	30.0	11.9	6.8	74.8

achieving 90% change in the full optical modulation at specified wavelength. The costing time of coloration (T_{color}) is 11.9 seconds by 90 % changing. Meanwhile, the bleaching time T_{bleach} is 6.8 s. The coloration/bleaching times are better than those reported in the other similar studies [19-22]. This result implies that Li^+ can quickly and easily intercalated/deintercalated in the WO_3 film. In fact, the response time is highly dependent on the diffusion coefficient of Li^+ and e^- will be exhibits a faster response [23]. In addition, the transparent electrode will be effect the response time. This is because the large number of electrons cause much current in the material with excellent conductivity, which will increase the charge-capacity of films. Higher charge-capacity indicates more Li^+ and e^- intercalation/extraction during the cyclic voltammetry process [24]. The comparison of electrochromic properties between the literatures and the proposed structure was summarized in Table 1. In addition, the tungsten trioxide of nano-crystalline structure has a high porosity, thus the electrons and lithium ions can be moved more quickly.

Fig. 6 shows the continuous potential cycling curves up to 100 cycles for WO_3 films. In the initial potential cycles, the coloring state gradually continues to increasing due to the electrolyte forming to solid-electrolyte inter-phase (SEI) adsorbed on the surface of the WO_3 film [25]. This process is called as activation effect. The cycling performance was saturated after a few initial cycling, referred to as the transient cycling period [26].

Conclusion

The $\text{WO}_3/\text{AZO}/\text{Ag}/\text{AZO}$ films were prepared by simultaneous RF magnetron sputtering (for WO_3 and AZO) and electron beam evaporation (for Ag). The conductivity of the transparent electrode (AZO/Ag/AZO films) on the electrochromic properties has been studied. The electrochromic device obtained the optical modulation (ΔT) of 74.8 % at 550 nm wavelength, the response time were obtained about 11.9 s (for colored stat) and 6.8 s (for bleached state). We achieved an excellent electrochromic device, that the advantages are large area, high contrast ratio in the visible range, faster response time and a long life-time. In addition, we have successfully developed a novel electrochromic device, which the device not only have high optical modulation but also IR-suppression for achieving simultaneously the properties of a high performance electrochromic device and low-E glass. This indicates that the AZO/Ag/AZO films to be a good candidate for high quality electrodes scheme in electrochromic devices applications.

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