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A novel all-thin-film electrochromic device for modulating optical transmittance

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An all-thin-film glass/ITO/WO_3/$LiAlO_2$/NiO_x/ITO device was successfully fabricated for electrochromic application, in which $LiAlO_2$ was used as the ion conducting layer material. The thin films were prepared by magnetron sputtering with a substrate temperature about -120 ℃. The film structure was characterized by X-ray diffraction (XRD), and the film morphology was characterized by scanning electron microscopy (SEM). The electrochromic properties of the films and the device were measured with cyclic voltammetry and spectrophotometry. For the obtained electrochromic device, the average visible light transmittances of bleached and colored state can reach 73.4% and 32.8%, respectively, and the optical transmittance modulation can reach 40.6%. The results indicated that the $LiAlO_2$ thin film was a suitable ion conductor for the electrochromic device, and the monolithic system glass/ITO/WO_3/$LiAlO_2$/NiO_x/ITO has great potential to be applied in smart windows.

Keywords: Electrochromic device, WO_3, NiO_x, $LiAlO_2$, Magnetron sputtering.

INTRODUCTION

Over the past decades, increasing attention has been paid to the reduction of energy consumption in residential and commercial buildings. Windows are a critical component of the building envelope which can greatly improve energy efficiency of buildings. Electrochromic (EC) devices can be used to modulate the throughput of visible light and solar energy in windows, as well as for other applications. The ability to control the energy flows through windows by EC devices (ECD) can lead to saving of huge power by reducing the demand for air conditioning, and this technology can also create comfortable working and living conditions [1–4]. To achieve optical modulation, as it is well known, the electrochromic thin film needs to be incorporated into a multilayer structure with layers for conducting electrodes, ionic conductor and ion storage. When a voltage of the order of few volts is applied between transparent electrodes, ions can be exchanged between the ion storage film and the electrochromic film, and the electrons injected from the transparent conductors then alter the optical properties. The coloration also can be stopped at any intermediate level, and the device exhibits open-circuit memory [5,6]. For applications, all-solid-state ECD have unique advantages such as reliability and safety, compared to conventional liquid-based devices in which liquid electrolytes are used as the ion conductors. There are two types of all-solid-state ECDs, laminated devices and all-thin-film devices. For a laminated device, the ion conductor is a polymeric electrolyte and the device consists of two half-cells laminated by the polymer. The polymeric electrolyte of a laminated device could have a degrading effect on the metal oxides, and produce problems like de-lamination and shrinkage. Compared to laminated devices, all-thin-film devices, in which the ion conductor is an inorganic film material, have received more attention because of their higher stability. A complementary ECD is a device containing two electrochromic layers, one of which is anodically colored while the other is cathodically colored, separated by an ion conducting layer.

In this study, a complementary all-thin-film transmittance-type EC device was successfully fabricated by a magnetron sputtering method, and its structure and performance were analyzed based on measurements. The device comprises a WO_3 film as the main cathodic electrochromic layer, a $LiAlO_2$ film as an inorganic ion conducting layer, a NiO_x film as a complementary anodic electrochromic layer, and a transparent conductive indium tin oxide (ITO) layer as the top and bottom electrode. The features of the ECD using $LiAlO_2$ film as ion conductor are low cost and high transmittance in bleached states.

EXPERIMENTAL DETAILS

All the films were prepared by a magnetron sputtering system. An ITO coated glass with a resistivity of 20Ω/m was used as the substrate. Sputtering took place from 6 cm diameter targets of

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W, Ni, $LiAlO_2$, and ITO. The W and Ni targets were of 99.9% purity. The $LiAlO_2$ target was prepared by ourselves using $LiOH·H_2O$ (99% purity) and Al_2O_3 (99% purity) with molar ratios 2: 1 [7]. The ITO target was In_2O_3-SnO_2 ceramic (90:10 by weight). The NiO_x and WO_3 films were prepared by DC magnetron sputtering at 100 W in a 3 Pa environment consisting of Ar and O_2 (flow rate of 70:30). The $LiAlO_2$ film was prepared by RF magnetron sputtering at 70 W in a 1 Pa environment consisting of Ar and O_2 (90:10 in rate of flow). The ITO film was prepared by RF magnetron sputtering at 70 W in a 1 Pa environment consisting of Ar. The ECD consisting of glass/ITO/WO_3/$LiAlO_2$/NiO_x/ITO was obtained, and the films thicknesses were 150/600/300/300/300 nm. During the deposition, the substrate was cooled by liquid nitrogen, and the substrate temperature was about -120℃.

The X-ray diffraction data of WO_3, NiO_x and $LiAlO_2$ films were recorded using Cu Kα radiation. The surface morphology of the WO_3 and NiO_x films was determined by scanning electron microscopy (SEM). The coloration characteristics of the ECD were characterized by spectrophotometry. The electrochemical properties of the WO_3 and NiO_x films were measured by cyclic voltammetry in a three-electrode electrochemical cell.

RESULTS AND DISCUSSION

Fig. 1 presents the XRD patterns of WO_3, $LiAlO_2$ and $NiOx$ films. We can see that the WO_3 and $LiAlO_2$ films are amorphous. Normally, amorphous and porous WO_3 films are more suitable than crystalline WO_3 films for EC applications, and the EC performance of the films is closely correlated with its structure and surface morphology [8-10]. Previous research suggested that amorphous ion conducting film is available as the solid electrolyte [11]. The amorphous $LiAlO_2$ thin film has very low Li^+ diffusion along in-plane direction, and this amorphous thin film can accept Li^+ intercalation and structural distortion. For the $NiOx$ film, a weak diffraction peak (200) was detected, and the peak at 43.36° was indexed as NiO [12]. Characteristic SEM images for the WO_3 and NiO_x films are shown in Fig. 2. It can be seen that the WO_3 particles are spheroidal, and their diameters are about 20 nm. The SEM micrographs indicated that WO_3 films exhibit fine particles and had an open porous surface structure. This character of the surface structure is crucial for the EC properties [9,13,14].

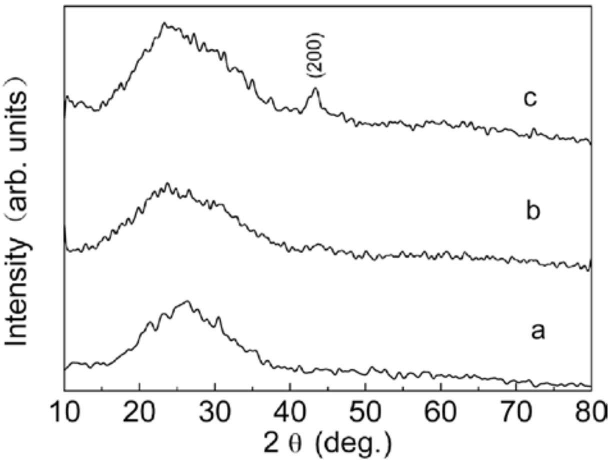

Fig. 1. XRD patterns of the as-deposited films: (a) WO_3, (b) $LiAlO_2$, (c) $NiOx$.

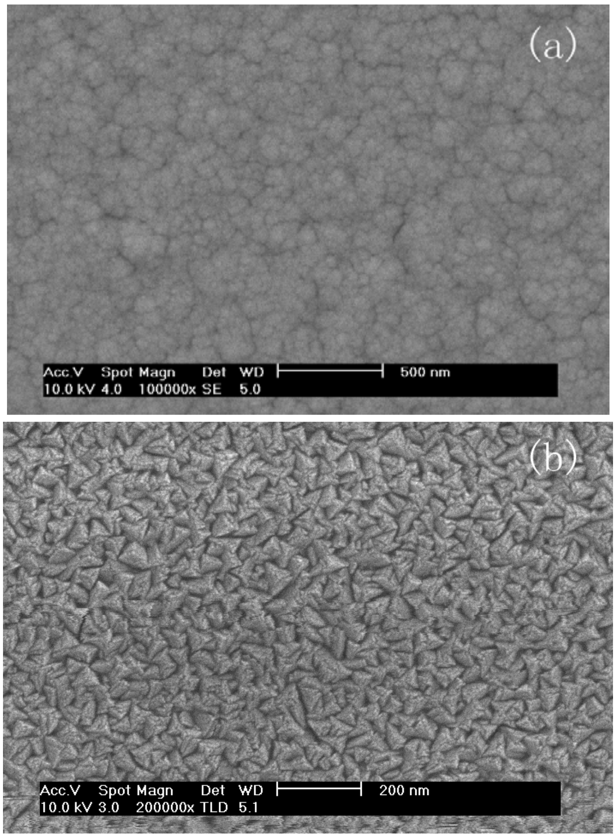

Fig. 2. Scanning electron microscopy surface images of films: (a) WO_3, (b) NiO_x.

The $NiOx$ is nano-crystalline, and the particle diameter is about 30 nm. Previous research showed that the electrochromic reaction occurred along the grain boundary of the $NiOx$ film, and small grain size would display a large surface to bulk ratio, which is important for high electrochromic activity [15].

The EC properties of the WO_3 and NiO_x films were mainly examined by cyclic voltammetry. The cyclic voltammograms of the films show the intrinsic shape of the electrochemical behavior and the charge densities related to continued Li^+

intercalation and deintercalation of the films [9,15]. Fig. 3 (a) shows the cyclic voltammograms of the WO_3 film. During cathodic potential scan from +2 to -1.9 V, current remains almost zero up to 180 mV, and further sharply increases, resulting in deoxidation of W^{6+} to W^{5+} and causing dark-blue coloration of the film, when the Li^+ ions and electrons flow into the film. Accordingly, the optical transmittance decays to reach a minimum at the voltammetric peak. Reversing the direction of the potential from -1.9 to 2 V, an anodic electric current is established and the film turns colorless when the Li^+ ions and electrons flow out of the film.

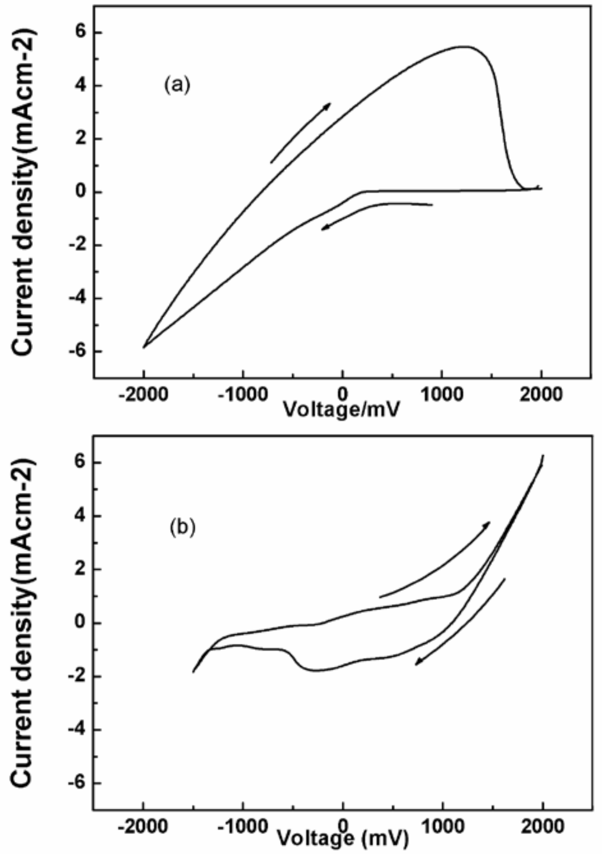

Fig. 3. Cyclic voltammograms of thin films: (a) WO_3, (b) NiO_x

Fig. 3 (b) shows cyclic voltammetric curves obtained during continuous potential cyclings for NiO_x film. The most remarkable feature of the cyclic voltammetric curves of NiO_x films is that a clear cathodic peak (+1.9 mA cm^{-2} at -345 mV) was observed in the cycle. The corresponding Li^+ ions and electrons flow into the film. During anodic potential scan from -1.9 to 2V, current density slightly increases up to 1129 mV and further sharply increases resulting in oxidation of Ni^{2+} to Ni^{3+}, consequently the color of the NiO_x film changes from transparent to brown. The slight current increase was related to the Li^+ ions and electrons flowing out of the film [16].

In order to examine EC property of the device, DC voltage of 5 V was applied at the top ITO electrode of the glass/ITO/WO_3/$LiAlO_2$/NiO_x/ITO stacked structure.

We propose the following mechanism for coloration of the EC device: The state of the ECD changes from as-deposited to colored when voltage is applied to the device such that the top ITO takes on a positive voltage. The state of the EC device changes to a bleached state after the applied voltage was switched off. The coloring and bleaching processes of the WO_3 and NiO_x films are due to the intercalation and deintercalation of Li^+ ions and electrons in the films according to the reactions (1), (2), and (3):

Cathodic coloring layer:

$$WO_3\ (\text{bleached}) + zLi^+ + ze^- \leftrightarrow Li_zWO_3,\ (\text{colored}) \quad (1)$$

Solid electrolyte layer:

$$LiAlO_2 \leftrightarrow x\ Li^+ + xAlO_2^- \quad (2)$$

Anodic coloring layer:

$$NiO_x(\text{colored}) + yLi^+ + ye^- \leftrightarrow Li_yNiO_x, (\text{bleached}) \quad (3)$$

Fig. 4 shows the visible light transmittance (T_{vis}) of the as-deposited, colored and bleached glass/ITO/WO_3/$LiAlO_2$/NiO_x/ITO device before and after voltage application. An integral over the whole spectrum can be calculated to describe the total optical transmittance [17]. The average transmittance in the wavelengths from 400 nm to 800 nm was 56.8% through the whole structure before applying the voltage. The absorption of visible light means a lower Ni^{3+} content in the as-deposited NiO_x thin film, and the Ni^{3+} content in the film can be improved by adjusting deposition conditions. As can be seen from the figure, the transmittance (T_{vis}) in the visible light range increases up to 73.4% through the structure after applying -10V on the top ITO electrode. By changing the polarity, the device became colored and the value of Tvis decreased to 32.8%. The T_{vis} modulation over the colored and bleached state was 40.6%. This value is comparable to that of the devices using other ion conducting materials, such as Ta_2O_5 and $LiNbO_3$ [18-20]. These results suggest that the ECD has a potential application for smart windows.

The *in situ* transmittance studies at 550 nm measured with respect to coloring and bleaching were used to calculate the response time. Fig. 5 shows the switching characteristics of the glass/ITO/NiOx/LiBSO/WO3/ITO ECD on application of a potential of ±5 V for five cycles.

The time taken for the film to color and bleach was obtained from these characteristics.

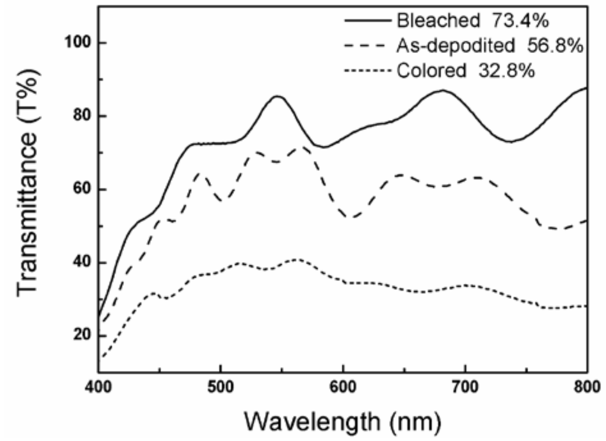

Fig. 4. Transmittance (T) of the glass/ITO /WO_3/$LiAlO_2$/NiO_x/ITO device

The coloration time is defined as the time required for the transmission of the film to decrease to 10% of the maximum transmittance value in the coloration cycle, and bleaching time is the time taken for the transmission to increase by 90% of the minimum value in the bleaching cycle. The maximum optical attenuation measured at 550 nm was 46%. Coloration time (T_c) and bleaching time (T_b) were found to be 20 s and 8 s, respectively, which are comparable to the other devices reported [21]. As the switching speed depends on the active area on which the material is deposited, the area was kept constant at 4 cm^2 for all measurements. The coloration time was longer than the bleaching time due to different color/bleach kinetics.

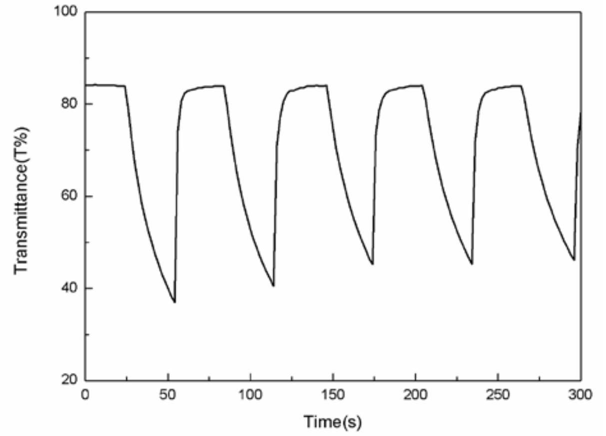

Fig. 5. Transmittance (at 550 nm) *versus* the response time of the device for five coloring and bleaching cycles.

CONCLUSIONS

In summary, a novel all-thin-film ECD employing WO_3 as the cathodically colored layer, NiO_x as the anodically colored layer, and $LiAlO_2$ as the ion conducting layer was fabricated by magnetron sputtering on an ITO/glass substrate. The $LiAlO_2$ film is electrochemically stable and avoids the problems generally associated with delamination and shrinkage seen in laminated devices using polymeric electrolyte. In addition, the $LiAlO_2$ film can be prepared easily and inexpensively, which is of interest to researchers involved in the development of inexpensive ECDs. The experimental results from the glass /ITO/WO_3/$LiAlO_2$/NiO_x/ITO are as follows: The transmittance in the visible light range of the device changed from 73.4% to 32.8% with the transmittance change (ΔT%) of 40.6%. Our results demonstrated that amorphous $LiAlO_2$ is available as a thin film electrolyte, which is particularly suitable for the low-cost and high-transmittance all-thin-film ECD. Further studies on the physical and electrochemical behavior are under way, to improve ΔT% values and cycle lifetime of ECDs.

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НОВО ЕЛЕКТРОХИМИЧНО УСТРОЙСТВО ОТ ИЗЦЯЛО ТЪНЪК ФИЛМ ЗА МОДУЛИРАНЕ НА ОПТИЧНА ПРОПУСКЛИВОСТ

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(Резюме)

Електрохимично устройство от изцяло тънък филм от стъкло/ITO/WO_3/$LiAlO_2$/NiO_x/ITO е произведено за електрохимично приложение, като $LiAlO_2$ е използван като йонно проводим слоест материал. Тънките филми са получени чрез магнетронно разпрашаване при температура на субстрата около -120 ℃. Структурата на филмите е охарактеризирана чрез рентгенова дифракция (XRD), а морфологията им – чрез сканираща електронна микроскопия (SEM). Електрохромните свойства на устройството са измерени чрез циклична волтамметрия и спектрофотометрия. Средната пропускливост на видима светлина на избеленото състояние и цветното състояние може да достигне съответно 73.4% и 32.8%, а модулирането на оптичната пропускливост може да достигне 40.6%. Установено е, че тънкият филм от $LiAlO_2$ е подходящ йонен проводник за електрохимичното устройство, а монолитната система стъкло/ITO/WO_3/$LiAlO_2$/NiO_x/ITO има голям потенциал за приложение в „интелигентни“ прозорци.