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A Reflective Inorganic All-Thin-Film Flexible Electrochromic Device with a Seven-Layer Structure *

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A reflective electrochromic device is fabricated on a 10 cm×10 cm flexible PI/Al substrate using magnetron sputtering. The device has a complementary all-thin-film structure and consists of seven layers. Indium tin oxide (ITO) acts as a transparent electrode deposited on the top, meanwhile, an aluminum (Al) film is adopted as an inter-counter bottom electrode and provides high reflectance. Tungsten oxide (WO_3) is used as the main electrochromic layer and nickel oxide (NiO) acts as the complementary electrochromic layer. Lithium niobate ($LiNbO_3$) is applied as a Li^+ ion conductor layer. Especially, in the seven-layer structure, two tantalum oxides (Ta_2O_5) are added as transition layers to prevent Li^+ escaping from $LiNbO_3$ when the potential is not applied on the device. When the device is in an electrochromic process, both Ta_2O_5 provide excellent conductivity for Li^+ ions and act as the dielectric of electrons. The complementary device with structure Al/NiO/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO exhibits good optical properties, and the reflectance modulation reaches up to 55% measured by a spectrophotometer in the range of 400–1600 nm. The cyclic stability of the electrochromic device is investigated. The results indicate that the charge density involved in the electrochromic process decreases and the electrochromic response time increases with the cycle number because of the Li^+ insertion in WO_3.

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Electrochromic devices (ECDs) have reversible change in their optical property (reflectance, transmittance) according to the applied voltage,[1,2] by means of alternate injection and extraction of small ions (such as Li^+ and H^+) and electrons.[3,4] Thus they have many potential applications in variable reflectance mirrors, information displays, smart windows, and optical switching devices.[5–7] The reflective ECDs generally consist of a transparent electrode, a cathodic colouration layer, an ion conductor electrolyte, an anodic colouration layer, and a bottom reflective electrode. The ion conductor can be liquid, polymeric, and solid inorganic thin films. The solid inorganic all-thin-film ECDs have attracted extensive attention owing to the advantages such as environmental stability, high reliability, and safety. The substrates of ECDs are mainly rigid, while more and more studies have focused on flexible ECDs because of their advantages such as relatively lower weight and cost, moreover, they have versatile shape ability.[8,9] Ta_2O_5 has been used in multilayered ECDs as an ion conductor electrolyte because of its high transmittance in the visible and UV range, low leakage current, high dielectric constant, excellent ions conductivity, and good chemical and thermal stability.[10,11] Considering applications of reflective ECDs, researches always focus on their reflectance modulation (ΔR) and durability.[12–14] Different from previous studies, in this work, Ta_2O_5 acts as a transition layer instead of an ion conductor layer, meanwhile, $LiNbO_3$ acts as an ion conductor layer.

Two Ta_2O_5 layers were added as transition layers to prevent Li^+ escaping from $LiNbO_3$ when the device was not in work. When the device had voltage applied in an electrochromic process, both Ta_2O_5 layers provide excellent conductivity for Li^+ ions and act as the dielectric of electrons. If the thickness of Ta_2O_5 was thinner than 100 nm, it cannot well prevent Li^+ escaping from $LiNbO_3$. However, a large thickness will hamper the movement of Li^+, and will lead to the response time of ECD being increased. Considering the above two reasons, the thickness of Ta_2O_5 was 150 nm.

A reflective inorganic all-thin-film ECD with the seven-layer structure of Al/NiO/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO was fabricated on a flexible PI substrate. The electrochromic properties including optical modulation and cyclic degradation were investigated.

An Al film was deposited on a PI substrate by roll-to-roll sputtering with the thickness of about 180 nm and a sheet resistivity of 2 Ω/square. Other layers were deposited on the 10 cm×10 cm flexible PI/Al substrate, which was fixed at the holder using magnetron sputtering at room temperature. Ni, Ta, $LiNbO_3$, W, and ITO targets were used to deposit the films. To prevent contamination, these Φ10 cm targets should be pre-sputtered for 10 min before the depositing process. During the deposition, the holder with the substrate rotated on its own axis. The device was fabricated layer by layer in sequence by the reactive magnetron sputtering system. The vacuum chamber was initially evacuated to a base pres-

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sure of 4×10^{-6} Torr. The gas flow of Ar (99.99%) and O_2 (99.99%) were adjusted individually by flow controllers. The gas pressure in the vacuum chamber was displayed timely. Deposition parameters of the multilayer ECD are listed in Table 1. The optical reflectance spectra were measured by a UV-VIS-NIR spectrophotometer (Lamda950) in the wavelength range of 200–2500 nm. The electrochemical property was evaluated by a cyclic voltammeter (CVs) and chronoamperometry (CAs).

Table 1. Deposition parameters of the multilayer ECD.

Film	Sputtering gas pressure (Pa)	Sputtering power (W)	Gas flow (cm^3/min)		Film thickness (nm)
			Ar	O_2	
NiO	3	90	70	30	500
Ta_2O_5	0.5	150	80	20	150
$LiNbO_3$	0.7	100	90	10	400
Ta_2O_5	0.5	150	80	20	150
WO_3	3	120	70	30	600
ITO	0.8	100	50	0	100

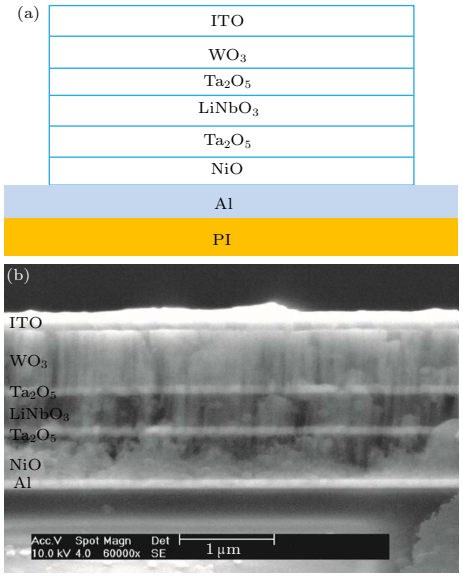

Fig. 1. (a) Schematic diagram of ECD and (b) SEM micrograph of cross section.

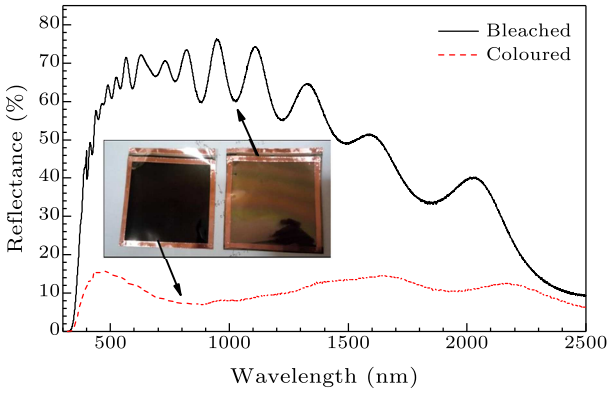

Fig. 2. Reflectance and photographs of bleached and colored states of the ECD.

The schematic diagram of the flexible multilayer ECD was exhibited in Fig. 1(a). The Al layer acts as a bottom electrode to connect with the applied voltage, thus the area has been reserved. In Fig. 1(b), the cross-section SEM (FEI Sirion at 10 kV) micrograph presents a seven-layer $Al/NiO/Ta_2O_5/LiNbO_3/Ta_2O_5/WO_3/ITO$ structure with a distinct interface. It is suggested that the interfacial reactions and diffusion do not occur in all the layers in the sequentially depositing process of the multilayer structure. The image is slightly misty, which is mainly due to the limitation of the sample preparation of flexible substrate.

Figure 2 shows the reflectance spectra of the ECD in the colored and bleached state. The applied voltage was −2.5 V/1.0 V for changing color at the largest extent and preventing the structure of ECD from destruction, simultaneously. The two photographs present the colored and bleached states, respectively. When the Li^+ ions were injected into the WO_3 layer and extracted from the NiO layer, the color of the ECD changes from bleaching to coloration spontaneously. The optical reflectance modulation (ΔR) of ECD is determined by

$$\Delta R = R_{\rm b} - R_{\rm c},$$

where $R_{\rm b}$ and $R_{\rm c}$ refer to the reflectances of bleached state and colored state, respectively. As shown in Fig. 2, the reflectances of the ECD are about 68.6% and 12.2% for the bleached and colored states at the wavelength of 530 nm, which are in the strongest wave range of solar radiation at air mass 1.5 on the earth surface. Correspondingly, ΔR is 56.4%, which is lower than the value of the five-layer ECD.[9] The lower optical modulation is mainly ascribed to the transition layers. The results of the spectrum show that the transmittance of $NiO/Ta_2O_5/LiNbO_3/Ta_2O_5/WO_3/ITO$ was lower than $NiO/LiNbO_3/WO_3/ITO$ when the ECD was in the bleached state. The reflectance ($R_{\rm e}$) of energy is generally adopted to evaluate the reflectance of solar radiation, and the formula is

$$R_{\rm e} = \frac{\int_{\lambda_1}^{\lambda_2} R(\lambda) E_{\rm s}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\rm s}(\lambda) d\lambda},$$

where $R(\lambda)$ is the tested reflectance of spectra, and $E_{\rm s}(\lambda)$ is the intensity of solar radiation at different wavelengths (λ). We can obtain the total solar irradiation reflectance when $E_{\rm s}(\lambda)$ spans over the solar irradiation spectra, while if $E_{\rm s}(\lambda)$ spans over the visible

spectra ($\lambda_1 = 390$ nm, $\lambda_2 = 780$ nm), the result will be visible reflectance.[15] The value of ΔR_e in the visible region (390–780 nm) is up to 51.2%. In addition, a higher ΔR_e of ECDs in the near infrared (NIR) region is more effective to energy efficiency properties for space applications and smart windows, because about half of thermal radiation energy concentrates in the wavelength range. As presented in Fig. 2, the calculated mean ΔR_e is nearly 55.7% in the wavelength from 780 nm to 1500 nm, and the highest modulation of spectra reflectance even reaches 68.4% at the wavelength of 946 nm. Obviously, the decline rate of R_b is great above 1500 nm from about 55% to 10%, which is mainly due to the intrinsic absorption of the Al electrode layer and the free-carrier absorption of the ITO electrode.[16]

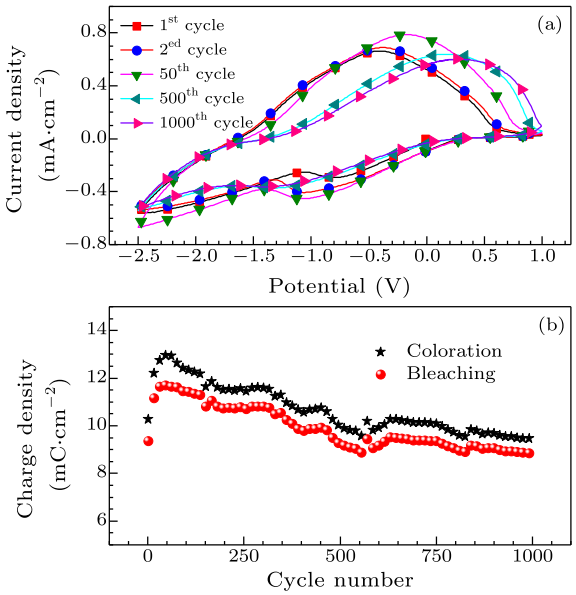

Fig. 3. (a) The CV curve and (b) charge density of different cycle numbers.

The CVs and CAs were adopted to evaluate the cyclic characteristic of the ECD. In Fig. 3(a), the area of the envelope gradually increases at first, indicating that more NiO and WO_3 were involved in the electrochromic process. With the cycle number increase, the area decreases gradually. This means that the charge density involving the electrochromic process decreases, as shown in Fig. 3(b), because of the Li^+ insertion in WO_3. The charge density is calculated with the area of the CV curve. It is indicated that the charge density in coloration is higher than bleaching. Considering that the leakage current is avoided efficiently, the unbalance of charge density is attributed to the different Li^+ quantities involved in the electrochromic process between insertion and extraction. In the coloring process, Li^+ could extract from NiO and insert in WO_3 efficiently because of the relatively higher voltage applied (−2.5 V). However, Li^+ could not extract from WO_3 totally at the relatively lower voltage (1 V).

The optical absorbance obtained timely is shown in Fig. 4. The ECD can obtain a steady absorbance modulation by means of adjusting the time of coloring and bleaching. The optical absorbance versus response time can indicate the response speed and cyclic stability of ECD. The time of coloring and bleaching degrades to 110 s and 70 s from 20 s after 10000 cycles, respectively. The reason is that some Li^+ inserted in WO_3 need higher applied voltages or longer applying time (in this study) to transfer into NiO.[17] The process will result in degradation of the response characteristic, and the response time increases with cycles. The Li^+ quantity involved in reversible transfer decreases because of Li^+ insertion in WO_3, which results in the transfer resistance correspondingly increasing. In addition, maybe the microstructure of WO_3 changes, which results from a high temperature of ECD and Li^+ insertion caused by multi-cycles. Together, the above processes result in response time increase of the ECD.

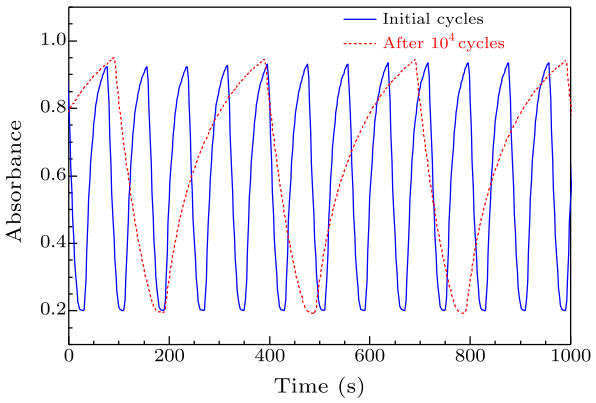

Fig. 4. Optical absorbance initially and after 10000 cycles.

In conclusion, a reflective inorganic all-thin-film flexible electrochromic device with the seven-layer structure of Al/NiO/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO has been fabricated by magnetron sputtering at room temperature. The device shows a high reflectance modulation up to 68.4% at a wavelength of 946 nm, thus could conserve energy efficiently. Meanwhile, the study on the cyclic characteristic indicates that the ECD has a relatively low charge density involving the electrochromic process after 10000 cycles, due to the fact that Li^+ inserts in WO_3. The response times individually increase to 110 s and 70 s from 20 s for the coloring and bleaching processes after 10000 cycles, because Li^+ inserted in WO_3 need longer applying time to transfer into NiO, and maybe the microstructure of WO_3 changes. This research confirms that seven-layer structure ECD has promising applications in excellent electrochromic performance, especially the cyclic stability is improved.

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