Charge-transfer kinetics and cyclic properties of inorganic all-solid-state electrochromic device with remarkably improved optical memory

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A B S T R A C T

Optical memory effect plays a critical role in energy-saving coefficient of electrochromic devices (ECDs). Due to the finite electron-blocking capacity of ions electrolyte layer and the weak interfacial energy between the ions electrolyte layer and electrochromic layers, typically five-layer inorganic all-solid-state ECDs generally suffer from poor optical memory. A seven-layer inorganic ECD with significantly improved optical memory is designed by means of the embedment of Ta_2O_5 layers between ions conductive layer and electrochromic layers. Compared with the typical five-layer ECD-1 ($ITO/NiO_x/LiNbO_3/WO_3/ITO$), the seven-layer ECD-2 with the structure of $ITO/NiO_x/Ta_2O_5/LiNbO_3/Ta_2O_5/WO_3/ITO$ presents much less leakage current, larger optical modulation and higher coloration efficiency during electrochemical cycling. The further analyses reveal that the embedded Ta_2O_5 layers greatly increase the energy barrier between NiO_x, WO_3 and $LiNbO_3$, imposing restrictions on the transfer kinetics of electrons contributing to the leakage current and enlarging the threshold potential available to ECD-2, which gives rise to a high coloration efficiency up to $98.0 \, cm^2 \, C^{-1}$. Furthermore, the seven-layer ECD-2 maintains a stable optical modulation of approximately 52.5% for over 10,000 cycles, even though there is a compromise in response characteristic due to the Li^+-ion trapping in electrochromic layers, which provides a further insight into the electrochromic degradation of inorganic all-solid-state complementary ECDs.

1. Introduction

With popularizing energy-efficient architectures and green buildings, electrochromic devices (ECDs), especially as smart window [1], have attracted extensive attention in the recent decades. Their effective optical modulation of incident light passing through windows is capable of implementing control over solar heat into architectures [2–5]. Electrochromism relates to the persistent switches between colored and bleached states of electrochromic materials under the reversibly simultaneous insertion/extraction of small ions (typically Li^+ and H^+) and charge-balancing electrons [6]. Accordingly, the transfer kinetics of these charges in coloring and bleaching processes plays a dominant role in electrochromic properties of ECDs [6], for instance, optical modulation, coloration efficiency, cyclic durability, especially response characteristic and optical memory (the ability to retain the optical transmittance in colored state of ECD under open-circuit condition) [7,8].

Inorganic all-solid-state complementary ECDs are typically composed of five superimposed layers: an ions electrolyte layer is laminated between two complementary electrochromic layers, cathodic colored tungsten trioxide (WO_3) and anodic colored nickel oxide (NiO_x), individually adjacent to a transparent conductive layer. However, such typically five-layer ECDs are usually subjected to poor optical memory, which would result in increased energy consumption [9]. Generally, the inorganic ions electrolyte layer suffers from relatively high electrons conductivity so that there is no effective restriction on the transfer of electrons in this layer. Furthermore, the relatively weak interfacial barrier energies between the ions electrolyte layer and the electrochromic layer lead to a low threshold of interfacial potential. Above the threshold, electronic leakage would be significantly transferred through the interfaces and, consequently, the optical modulation of ECDs is obstructed. Therefore, both the electron-blocking capacity of ions electrolyte layer and the interfacial barrier energies dominate the threshold potential applied between two electrodes of the ECDs, which plays a decisive role in the maximum optical density of the ECDs with a given multilayer structure.

Taking energy conservation into consideration, the introduction of proper electron-blocking buffer layers such as ZrO_2, Ta_2O_5 and SiO_2 into these typical ECDs is requisite for improving optical memory. Among them, Ta_2O_5 thin films serving as protective layers from dissolution and resultant degradation of WO_3 and $Ni(OH)_2$ in ECDs based on H^+-ion polymer electrolyte showed a good ions-transfer kinetics [10,11]. Its electron-blocking behavior, high ions conductivity and chemical stability give impetus to its investigation as capacitor insulators in electronic devices, solid ions conductive layers and protective layers in electrochromic devices [10–18]. It seems that Ta_2O_5 is a promising electron-blocking buffer layer for reducing the amount of electronic leakage and improving the optical memory and the optical modulation of ECDs. Currently, there are a lot of reports with respect to the studies on electrochromic properties of inorganic all-solid-state ECDs [17–23]. However, the majority focused on optical contrast ratio, coloration efficiency and response rate, while paying less attention to charge-transfer kinetics, optical memory and cyclic properties as a function of number of cycles. Practically, the variation of physical and chemical properties is unavoidable for electrochromic materials resulting from the continual switches between colored and bleached states [24,25], which, in return, could lead to evolutions of cyclic properties of ECDs.

The present work focuses on improving the optical memory of inorganic all-solid-state ECD via incorporating two Ta_2O_5 buffer layers as electron-blocking layers and its cyclic properties versus number of cycles. A seven-layer complementary ECD-2 (ITO/NiO_x/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO) is designed and prepared by magnetron sputtering method. Another ECD-1 with typically five-layer structure (ITO/NiO_x/$LiNbO_3$/WO_3/ITO) is prepared for comparison. Cyclic voltammograms (CVs), chronoamperograms (CAs) and their derived results are analyzed for studying the charge-transfer kinetics of both ECDs. The analysis unambiguously reveals the negative effect of electronic leakage on the electrochromic properties of ECD-1 and indicates the excellent electron-blocking capacity of Ta_2O_5 layers in ECD-2. A remarkably improved optical memory effect occurs to the ECD-2 as a result of the embedment of two Ta_2O_5 layers, which also can provide a new approach to the leakage current of other electronic devices originating from the interfaces imperfections, for example, solar cells. Besides, we demonstrate the cyclic properties of the ECD-2, including the evolutions of its CV cycles versus number of cycles and coloration efficiency. The study on deteriorating response characteristic of ECD-2 with a stable optical modulation brings a further insight into the degradation of ECDs.

2. Experimental details

2.1. Preparation of inorganic all-solid-state ECDs

Inorganic all-solid-state ECD-1 (ITO/NiO_x/$LiNbO_3$/WO_3/ITO) and ECD-2 (ITO/NiO_x/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO) were individually prepared on the 3 cm × 5 cm ITO-coated glass substrates layer by layer using magnetron sputtering at room temperature. Previously, these ITO-coated substrates with a sheet resistance of 25 Ω cm^{-2} were successively ultrasonically cleaned in anhydrous ethanol and deionized water for 20 min, and then one 10 mm edge of them was masked with vacuum tape as working electrode after dried in ambient air. The corresponding target with the diameter of 100 mm was pre-sputtered for 10 min in order to prevent cross-contaminants prior to the deposition of every single layer. In the processes of preparation, the holder was rotated at a certain speed and the vertical distances between targets and substrate are approximately 150 mm. The vacuum chamber was initially pumped to a base pressure of 3.0×10^{-3} Pa. The flow rates of Ar (99.99%) and O_2 (99.99%) were adjusted individually by mass flow controllers. More details on deposition parameters of both ECDs are presented in Table 1. For the characterization of optical transmittance of single Ta_2O_5 and $LiNbO_3$ layers, both were deposited on glass substrates without coated ITO, respectively. Besides, Au thin film, $LiNbO_3$

Table 1
Detailed deposition parameters of all layers assembled into the all-solid-state ECDs.

Layer	Target	Power source	Working pressure (Pa)	Ar:O_2 (sccm)	Power (W)
NiO_x	Ni	DC[a]	1.5	400:35	250
Ta_2O_5	Ta	DC	0.3	140:60	280
$LiNbO_3$	$LiNbO_3$	DC	0.6	190:10	150
WO_3	W	DC	2.0	300:100	300
ITO	ITO	DC	0.3	270:12	180

[a] Direct current.

layer and 2nd Au thin film were successively prepared on a glass substrate (Glass/Au/$LiNbO_3$/Au) for the measurement of electrochemical impedance spectroscopy (EIS) of $LiNbO_3$ layer.

2.2. Characterization of structural and chemical properties

Structural profile of the as-prepared ECDs was examined with cross-sectional images obtained by high-resolution FEI-Phillips XL30 S-FEG emission scanning electron microscopy (SEM) operating at 10 kV. The chemical composition of the Ta_2O_5 thin film was measured by X-ray Photoelectron Spectroscopy (XPS) (Physical Electronics PHI-5600 system) using monochromatic Mg Kα (1253.6 eV), operating at 200 W. High-resolution spectra of Ta 4f and O 1s were acquired with a five scans accumulation. A Shirley background was removed for the calculation of the elementary composition of O 1s peak. The standard C 1s at 284.6 eV was applied for the calibration of binding energy. Crystallographic property of Ta_2O_5 thin film was characterized by GIXRD (M189XHF-SRA, Mac Science) with Cu Kα (λ = 1.5405 Å) at a constant incidence angle of 0.5°.

2.3. Electrochemical and optical measurements

The optical transmittance spectra of ECDs were acquired at a scanning speed of 300 nm min^{-1} in the range from 350 nm to 800 nm by ultraviolet-visible (UV–vis) spectrophotometer (HITACHI UV-3010) with transmittance model (T% model). The *In-situ* optical transmittance of the ECDs versus time was acquired at 550 nm and the air was used as the baseline and reference. The optical transmittance of single Ta_2O_5 and $LiNbO_3$ layers was acquired using a glass substrate as the baseline.

The electrochemical measurements for these ECDs were implemented with a two-electrode cell in a CHI 660E electrochemical workstation (CH Instruments) at room temperature. For these measurements, the top ITO layer adjacent to WO_3 layer was used as the working electrode, and the bottom ITO layer next to NiO_x layer was connected to the counter electrode linking to the reference electrode. Prior to these characterizations of the ECD, 1–2 mm width of all edges except the masked edge with vacuum tape was cut off for prevention from leakage current caused by edge shorts. The electrochemical impedance measurements of $LiNbO_3$ layer (1 mm^2) was performed in the frequency range 0.1 Hz – 1 MHz.

3. Results and discussion

3.1. Physical structure of ECDs and properties of Ta_2O_5 layers

Fig. 1 illustrates the physical structure of ECDs based on their cross-sectional images, crystalline property and chemical composition of corresponding Ta_2O_5 layers. As seen in Fig. 1a, the ECD-1 displays a typically five-superimposed structure of ITO/NiO_x/$LiNbO_3$/WO_3/ITO. For the ECD-2, there is a seven-layer structure of ITO/NiO_x/Ta_2O_5/$LiNbO_3$/Ta_2O_5/WO_3/ITO with sharp interfaces between adjacent layers shown in Fig. 1b. Except the embedded Ta_2O_5 layers, all layers in ECD-2 exactly have the same uniform thickness (690 nm for WO_3, 400 nm for $LiNbO_3$ and 550 nm for NiO_x, respectively) as the corresponding layers