Thickness dependent surface roughness of sputtered $Li_{2.5}TaO_x$ ion conductor and its effect on electro-optical performance of inorganic monolithic electrochromic device

Yu Xiao, Guobo Dong, Junji Guo, Qirong Liu, Qingjiao Huang, Qianqian Zhang, Xiaolan Zhong, Xungang Diao[*]

School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, PR China

ARTICLE INFO

ABSTRACT

Transparent amorphous $Li_{2.5}TaO_x$ thin films with different thicknesses were deposited by RF magnetron sputtering. The ionic conductivities of as-deposited films determined by ac impedance spectroscopy were of the order of 10^{-8} S/cm at room temperature. The surface roughness increased rapidly with the film thickness increasing as confirmed by scanning electron microscopy and atomic force microscopy. Inorganic monolithic electrochromic devices (ECDs) based on $WO_3//NiO$ complementary structure were fabricated using the $Li_{2.5}TaO_x$ with different thicknesses as the ion conductor layers. The electro-optical performance of the ECDs was characterized by cyclic voltammetry and chronoamperometry. The ECDs showed a highest optical modulation of 40% at 550 nm driven by − 1.5 V (coloration) and 1 V (bleaching) with switching time of 30 s. Both the amount of transferred charge and coloration efficiency were found to be highly dependent on the film thickness of $Li_{2.5}TaO_x$ layer. The high charge transfer resistance at the $Li_{2.5}TaO_x/WO_3$ interface and poor growth of WO_3 layer due to the high surface roughness of $Li_{2.5}TaO_x$ may well account for the decreased device performance.

1. Introduction

Electrochromic devices (ECDs) for energy-efficient architectural windows known as "smart windows" have drawn considerable attention from academia and industry over the last decades [1–9]. They provide a viable option for dynamic control of visible light and solar energy leading to life comfort and energy saving.

The use of inorganic thin films presents plenty of advantages for practical implementation of EC smart windows, e.g., continuous in-line large area manufacturing possibility, no bubble formation, expected high durability under a wide range of temperatures or ultraviolet radiation. Many efforts have been devoted on investigations of transparent conductors [10], EC active electrodes [11–15], and ion conductors [16–18]. Device performance and durability have been widely studied as well [19–21]. Some companies have developed their own EC windows products (e.g., SageGlass, View, or Asahi Glass). However, it is still a semi-commercial scale market and the long-term durability still needs to be examined. There are many scientific questions remained to be studied. For instance, Wen et al. have discussed the ion-trapping-induced degradation of WO_3 thin films [22]. Recently, Oukassi et al. have reported that interactions between the depositing and the deposited layers would influence the total amount of injected charges during the deposition processes of a thin film monolithic device [4].

The electrochromic phenomenon is based on intercalation/deinter-calation of small ions (especially Li ions) in EC active electrodes. The device performance can vary substantially according to multilayer structure, film thickness, or switching voltage. During the coloration and bleaching of an ECD, Li ions will transport through the electrolyte and electrolyte/electrode interface, and then intercalate into the electrode. Therefore, the Li transport dynamics must play an important role in affecting the device performance. To our knowledge, little attention has been focused on the solid-solid electrolyte/electrode interface in solid monolithic ECDs, whereas the charge transfer resistance at the electrolyte/cathode interface has been extensively investigated in solid Li battery systems [23–25]. A good solid-solid interface with low interfacial resistance allows a high degree of reversibility and stability.

In this work, the $Li_{2.5}TaO_x$ thin films with different thicknesses prepared by RF magnetron sputtering were used as the ion conductor layers in the ECDs. The structural, morphological, optical and electrical properties of $Li_{2.5}TaO_x$ thin films were characterized. The device performance was evaluated by cyclic voltammetry and chronoamperometry with in situ transmittance recording. The effects of

---

thickness dependent surface roughness of the $Li_{2.5}TaO_x$ layer on device performance were discussed.

2. Experimental

2.1. Deposition of $Li_{2.5}TaO_x$ thin films

The $Li_{2.5}TaO_x$ thin films were deposited by RF magnetron sputtering from a $LiTaO_3$ target with a diameter of 10 cm and thickness of 6 mm. Silica glass, silicon wafer, and ITO-coated glass were used as the substrates. The substrates were not intentionally heated nor cooled during the deposition. The target-to-substrate distance was 15 cm. Prior to the deposition, the chamber was evacuated to a base pressure lower than 1×10^{-3} Pa. The target was pre-sputtered in an argon atmosphere for 20 min in order to remove the surface contaminations. During deposition, the gas flow ratio of O_2/Ar was set at a constant value of 5%. The total pressure was maintained at 0.8 Pa. The sputtering power was kept at 300 W corresponding to a power density of 3.82 W/cm². $Li_{2.5}TaO_x$ thin films with different thicknesses ranging from 140 to 1250 nm were deposited by setting the deposition time as 1, 2, 3, 5, and 8 h. Film uniformity was guaranteed by substrate rotation during the sputtering.

2.2. Deposition of the electrochromic devices

The ECDs studied in this work consisted of WO_3 and NiO as the EC active layers, $Li_{2.5}TaO_x$ as the ion conductor, and two ITO electrodes as the transparent conductors. All the layers of the ECDs were deposited by DC or RF sputtering. The deposition of each layer was performed continuously in a multi-target magnetron sputtering system without breaking the vacuum. Each target was equipped with a cover to avoid cross contamination. Pre-sputtering took place in pure argon for 20 min before each deposition. The base pressure of the chamber was evacuated to lower than 1×10^{-3} Pa. ITO-coated glass having a sheet resistance of 30 Ω and an average transmittance of 85% in the visible region was used as the substrate. The target-to-substrate distance was 15 cm. No substrate heating was used during the deposition. The sample holder kept rotating to obtain homogeneous thin films. The sheet resistance of the top ITO layer prepared in this work was around 40 Ω. The detailed sputtering conditions for WO_3, NiO, and top ITO layers are listed in Table 1. For each device configuration, 4 samples were prepared in order to guarantee reproducibility. The active size of the ECDs was 5×5 cm². Detailed device configurations are shown in Table 2.

2.3. Characterization

Film structures were determined by grazing incidence X-ray diffraction (GIXRD) using a Rigaku D/MAX-2500/PC diffractometer with a Cu Kα source. The incidence angle was 0.5°. Diffraction scan was run from 10° to 90° 2theta with a step of 0.05° and a step time of 0.1 s. The Raman measurements on $Li_{2.5}TaO_x$ films were carried out using a WITec alpha300R spectrometer with a 532 nm excitation source. The atomic ratio of Li/Ta was acquired from ICP-OES analysis using a Vista-MPX from Varian. The films were dissolved in concentrated HNO_3

Table 1
Deposition conditions for the WO_3, NiO, and top ITO layers of the electrochromic devices.

Film	Target	Power density (W/cm²)[a]	O_2/Ar (sccm)	Pressure (Pa)	Thickness (nm)	t_d (min)[b]
WO_3	W	DC, 4.2	10/30	2	400	10
NiO	Ni	DC, 3.2	6/94	3	200	20
ITO	ITO	DC, 2.7	1/99	0.3	250	20

[a] DC refers to direct current power source.

[b] t_d stands for deposition time.

Table 2
Multilayer configuration for the electrochromic devices with $Li_{2.5}TaO_x$ ion conductor.

Sample no.	Device configuration[a]	Ion conductor layer		T_{max} (°C)[c]
		Thickness (nm)	t_d (h)[b]	
ECD-1	G/ITO/NiO/LTO/WO₃/ITO	140	1	45
ECD-2	G/ITO/NiO/LTO/WO₃/ITO	300	2	50
ECD-3	G/ITO/NiO/LTO/WO₃/ITO	445	3	53
ECD-5	G/ITO/NiO/LTO/WO₃/ITO	755	5	57
ECD-8	G/ITO/NiO/LTO/WO₃/ITO	1250	8	59
ECD-8r	G/ITO/WO₃/LTO/NiO/ITO	1250	8	61

[a] G represents glass substrate and LTO represents $Li_{2.5}TaO_x$ film.

[b] t_d stands for deposition time of the ion conductor layer.

[c] T_{max} stands for maximum temperature measured at the substrate during multilayer deposition.

solution, and then diluted to 3%. ATR-FTIR spectra from 2000 cm⁻¹ to 675 cm⁻¹ were acquired using a Nicolet iN10 MX FTIR microscope (Thermo Scientific Inc.). The surface morphologies were analyzed by a scanning electron microscope (SEM, XL30 S-FEG from FEI) and atomic force microscope (AFM, Dimension from Bruker). The thickness of the $Li_{2.5}TaO_x$ films measured by a stylus profiler (Dektak 6M) agreed well with the cross-sectional SEM observations. Optical transmittance spectra of the $Li_{2.5}TaO_x$ films were measured at the wavelength range of 200–1100 nm.

Electrochemical impedance measurements for ionic conductivities of the $Li_{2.5}TaO_x$ thin films were conducted at room temperature (25 °C). An ac voltage with 100 mV amplitude was applied on the glass/stainless steel/$Li_{2.5}TaO_x$/stainless steel sandwich structures. The frequency ranged from 0.1 Hz to 1 MHz. The active electrode area was 2 mm². 6 samples were independently measured for the $Li_{2.5}TaO_x$ films with each thickness to reduce errors. The partial electronic conductivity has been measured by dc current decay curves under a constant voltage of 2 V. The polarization time was 1000 s.

The ECDs were electrically characterized based on cyclic voltammetry (CV) and step chronoamperometry (CA). The electrical data were recorded with a CHI600E electrochemical workstation. The potential window was − 1.5 V (coloration) and 1 V (bleaching) for both CV and CA measurements. The initial cycling of the as-deposited ECD was carried out by CV at a scan rate of 20 mV/s. Each CV measurement was performed for 50 cycles, and then the ECDs were subjected to CA measurements for 300 cycles. The duration was 30 s for coloring step and 30 s for bleaching step in CA cycles. The optical transmittance data (at 550 nm) were acquired in situ during the electrochemical cycling of the ECDs. Finally, the open circuit memory tests were carried out after the ECDs were colored to the same tinted level (30% at 550 nm) driven by − 1.5 V. The transferred charge (ΔQ) was derived from CV data by

$$\Delta Q = \int \frac{j\mathrm{d}V}{s}$$

where j is current density, s is scan rate, and V is voltage. Coloration efficiency (CE) is defined as the change of optical density (ΔOD) at a certain wavelength per unit of inserted (or extracted) charge density (ΔQ). The formula is defined as follows:

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{\Delta Q}$$

$$\Delta OD(\lambda) = \log(\frac{T_b}{T_c})$$

where T_b and T_c refer to the bleached and colored transmittance, respectively.