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Electrochemical studies of silicon nitride electron blocking layer for all-solid-state inorganic electrochromic device

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ABSTRACT

All-solid-state inorganic electrochromic devices (ECD) typically suffer from the leakage current which mainly arises from bulk defects and pinholes particularly in the ion conducting layer. The leakage current can lead to rapid self-bleaching of the ECD under open circuit, increased power consumption, and inhomogeneous coloration. Silicon nitride (Si_3N_4) thin films were prepared by pulsed DC reactive magnetron sputtering, and integrated into a monolithic inorganic ECD to reduce the leakage current. The device was prepared by a series of sputtering processes and the layer stacks were Glass/ITO/NiO/Si_3N_4/$LiNbO_3$/Si_3N_4/WO_3/ITO. The optimization of Si_3N_4 single layer was studied by electrochemical cyclic voltammetry. The effects of leakage current on electrical and optical properties of the ECDs were studied by chronoamperometry and cyclic voltammetry. The leakage current of the device is reduced from 216.0 to 32.1 $\mu A/cm^2$ with two 80nm-thick Si_3N_4 layers, and the open circuit memory effect is significantly improved. The optical modulation is 43% at 550 nm by applied voltages of −2.0 V and 1.5 V.

1. Introduction

Electrochromic devices (ECD) have been extensively investigated for many potential applications such as skylights, optical displays, smart energy-efficient windows, and rearview mirrors [1,2]. They have attracted considerable technological and commercial interests due to their unique properties of switching optical transmittance upon the insertion/extraction of small ions and electrons [3–5]. The conventional superimposed ECDs contain a five-layer structure: an ion conducting layer sandwiched by an electrochromic (EC) layer and an ion-storage layer which are individually deposited on transparent electrodes [6–8]. EC layer materials can be divided into two categories: cathodic and anodic coloration materials. Among the inorganic cathodic colored materials, WO_3 is considered as the most desirable candidate for the EC layer owing to its high coloration efficiency, large dynamic range, and good cyclic reversibility [9–12]. Anodic colored NiO_x is regarded as a promising material complementary to the cathodic colored WO_3 [13,14].

Electrochromic device employing an inorganic electrolyte may present considerable advantages compared to ECDs having liquid or polymer gel electrolytes, especially concerning physical and electrical durability [15–17]. However, a major concern with monolithic inorganic ECDs is the inherent leakage current that mainly arises from the pinholes and structural imperfections, particularly in the ion conducting layer[18]. The leakage current usually generates negative effects on electrochromic properties of the ECDs such as a lowered dynamic range, inhomogeneous coloration, decreased ionic conductance, slower switching speed, and increased power consumption. It is reported that the yearly energy consumption can be estimated to be 4 KWh/m^2 for a leakage current of 100 $\mu A/cm^2$ [19,20]. Leakage current can reduced by increasing the thickness of ion conducting layer [21]. The tantalum oxide (Ta_2O_5) thin films of 300 nm thick as electrolyte to improve the leakage current has been examined by Wang et al. [15]. Unfortunately, it is expense of degraded optical properties, increased layer deposition time and cost. However, the Si_3N_4 thin film of only 80 nm thick as a electron blocking layer in ECDs with I^-/I_3^- and TMTU/TMFDS^{2+} based redox electrolytes reduced the leakage current from 240 to 20 $\mu A/cm^2$,which has been studied by Bogati et al. [19].

The aim of this work is to present some results of applying Si_3N_4 as electron blocking layers for all-solid-state inorganic electrochromic device. The Li ion conducting properties of Si_3N_4 thin films influenced by various sputtering conditions were investigated by cyclic voltammetry. Electro-optical characterizations were carried out to evaluate the performance of the ECDs with and without the

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Si_3N_4 layers. The effects of leakage current on the electrical and optical properties of the ECDs were studied in detail.

2. Experimental

2.1. Deposition of Si_3N_4 thin films

The Si_3N_4 thin films were deposited on WO_3/ITO-coated glass substrates by pulsed DC reactive magnetron sputtering in a mixture gas of argon and nitrogen. Here all these WO_3 substrates were prepared at the same sputtering conditions. The target was 100 mm in diameter SiAl plate with a thickness of 6 mm. Prior to the deposition, the ITO-coated substrates were ultrasonically cleaned in anhydrous ethanol for 15 min. The distance between target and substrate was 15 cm. The base pressure was 1×10^{-3} Pa evacuated by a turbo molecular pump combined with a rotary pump. The SiAl target was pre-sputtered in pure Ar atmosphere for 5 min to remove surface contaminant. The gas flows of Ar (99.99%) and N_2 (99.99%) were adjusted individually by mass flow controllers. The nitrogen partial pressure ratio was defined as $PN_2 = P(N_2)/[P(N_2) + P(Ar)]$, where $P(N_2)$ and P(Ar) were the gas pressures of the N_2 and Ar, respectively. PN_2 was varied from 10% to 40%. The working pressure was adjusted from 0.3 to 2.0 Pa. During the deposition process, the pulsed DC power was maintained at 275 W with a pulse duty ratio of 70%. The deposition time was controlled in order to prepare films with thickness of 40, 80, 120, 260, and 320 nm. All the samples were deposited at room temperature.

2.2. Preparation of all-solid-state inorganic electrochromic devices

Inorganic all-solid-state ECDs based on complementary WO_3 and NiO electrochromic active electrodes were sputtered layer by layer on ITO-coated glass substrates, and the ECDs with and without Si_3N_4 electron blocking layers were prepared. The multilayer structures can be depicted as Glass/ITO/NiO/Si_3N_4/$LiNbO_3$/Si_3N_4/WO_3/ITO and Glass/ITO/NiO/$LiNbO_3$/WO_3/ITO, respectively. Detailed experimental parameters of the ECDs are listed in Table 1. It is deserved to mention that the ion conducting layer was prepared by DC reactive magnetron sputtering from an oxygen-deficient $LiNbO_3$ conductive target. The application of DC sputtering power can effectively increase the deposition rate compared with RF sputtering power, more importantly, make it possible for industrial large scale production.

2.3. Characterization

Film thickness was determined by surface profilometry using a Dektak instrument. The surface roughness of films was measured using a Veeco Dimension 3100 instrument employed in tapping mode. Film structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX-2500/PC diffractometer with a Cu Kα source. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a VG Scientific ESCALab Mark II photoelectron spectrometer. Peak shifts due to charging were normalized by fixing the C 1s peak to 284.6 eV. The cross-sectional image of the ECD was obtained by scanning electron microscopy (SEM) using a XL30 S-FEG from FEI. The Si_3N_4 thin films deposited on WO_3/ITO/glass substrates were subjected to the cyclic voltammetry (CV) test. A three electrode cell configuration was set up containing 1 M $LiClO_4$-PC solution as the electrolyte, ITO as a working electrode, Ag/AgCl as a reference electrode, and platinum foil as a counter electrode. The measurements were carried out using a CHI660E electrochemical workstation. Cyclic voltammograms were acquired at a scan rate of 20 mV/s with sweeping from −1.0 V to 1.0 V. For the complete device, the CV cycles were performed at a scan rate of 50 mV/s between −2.0 V and 1.5 V. Step chronoamperometry (CA) cycles were conducted under −2.0 V for coloration and 1.5 V for bleaching. The duration of each step was 30 s. The optical transmittance spectra of the ECDs were measured in situ by a Hitachi U-3010 UV–vis spectrophotometer at a wavelength of 550 nm. The transmittance spectra of the device at its original, colored, and bleached states were measured over a wavelength of 300–800 nm.

3. Results and discussion

3.1. Characterization of Si_3N_4 thin films

Fig. 1 illustrates characteristic topographies for Si_3N_4 films prepared at various N_2 contents. The root mean square roughness (Rq) decrease first and then increase in general as the N_2 contents. The values of Rq are respectively 3.17, 2.70, 2.74, and 3.29 nm, corresponding to N_2 content of 10%, 20%, 30%, and 40%. The minimum value appears when the N_2 content equals 20%. The as-deposited Si_3N_4 films are smooth which would facilitate Li ion transportation and film growth for top layers of the ECD.

The Li ion conducting properties of Si_3N_4 thin films were evaluated by cyclic voltammetry (CV) test conducted in 1 M anhydrous $LiClO_4$-PC solution. The Si_3N_4 thin films prepared at various parameters were deposited on WO_3/ITO/glass substrates. The considered sputtering conditions were N_2 content, working pressure, and film thickness. The WO_3 substrates were prepared at the same parameters, which were shown in Table 1. CV curves showed the intrinsic electrochemical behavior of WO_3. By coating Si_3N_4 thin films prepared at different parameters, the peak current density and charge density of the CV curves changed. The charge density (area of the CV curve) reflects the optical contrast of the WO_3 thin film, and the cathodic (anodic) peak current density is related with the Li ion intercalation (deintercalation) diffusion coefficient, which only depends on the Li ion conductivity of the Si_3N_4 thin film due to the same WO_3 electrochromic active layer. In this work, the diffusion coefficients of Li ions were calculated by using Randles-Sevick equation [22,23]:

$$i_p = 2.72 \times 10^5 \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C_0 \times \upsilon^{\frac{1}{2}} \qquad (1)$$

where D is the diffusion coefficient, C_0 is the concentration of active ions in the solution, ν is the scan rate, n is the number of electrons and is assumed to be 1, i_p is the peak current density.

Table 1
Deposition parameters of the electrochromic devices.

Target	Power source	Pressure (Pa)	Ar:O_2:N_2 (sccm)	Power (W)	Sputtering time (min)	Thickness (nm)
Ni	DC	3	94:6:0	236	30	320
SiAl[a]	Pulsed DC	0.5	40:0:10	275	6	80
$LiNbO_3$	DC	0.8	95:5:0	152	60	130
W	DC	2.2	27:9:0	303	10	330
ITO	DC	0.3	78.4:1.6:0	180	20	250

[a] Composition of the SiAl alloy target: 90 wt.% Si, 10 wt.% Al.