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Electrochromic performance of PECVD-synthesized WO_xC_y thin films on flexible PET/ITO substrates for flexible electrochromic devices

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ABSTRACT

Electrochromic performance of WO_xC_y films deposited onto 60 Ω/□ flexible PET (polyethylene terephthalate)/ITO (indium tin oxide) substrates by low temperature plasma-enhanced chemical vapor deposition (PECVD) was investigated. It was proven that extraordinary electrochromic performance was provided when the precursor [tungsten carbonyl, $W(CO)_6$; TC] vapor, carried by argon gas, was mixed with air gas and synthesized by radio frequency (r.f.) power at room temperature (23 °C). Cyclic voltammetry switching measurements found that only low driving voltages from −1 V to 1 V were needed to provide reversible Li^+ ion intercalation and de-intercalation. The light modulation with up to 63.6% of transmittance variation at a wavelength of 650 nm was obtained for 150 cycles of Li^+ intercalation and de-intercalation in a 0.1 M $LiClO_4$-PC (propylene carbonate) electrolyte.

1. Introduction

Commercial interest in electrochromic devices (ECDs) has centered around three main types of product: displays, mirrors and windows [1]. Several companies and major glass manufacturers have built laminated or monolithic demonstration devices on glass. Electrochromic devices on flexible substrates have been investigated for the specific advantage of having versatile shapability. Since the discovery of the electrochromic phenomenon in tungsten oxide films [2], this material has remained the most promising candidate for large-scale uses of electrochromic devices. It is generally accepted that WO_{3-z} film in a bleached state (colorless) can be reversed to a colored state (dark-blue) by intercalation of ions and electrons to form tungsten bronze (M_xWO_{3-z}) according to the intercalation/de-intercalation reaction (Eq. 1) [3]:

$$WO_{3-z} + xM^+ + xe^- \leftrightarrow M_xWO_{3-z} \tag{1}$$

where M^+ denotes H^+, Li^+, Na^+ or K^+ ions.

Garg et al. [4] pointed out that the advantages of PECVD over sputtering are dominated by potentially higher deposition rates that results in a cost of depositing for tungsten oxide films. PECVD was a factor of 3 lower than for sputtering. PECVD of electrochromic tungsten oxide films was first demonstrated by Tracy and Benson in 1986 [5], and confirmed by Kuypers et al. in 1995 [6]. Henley and Sacks in 1997 [7] qualitatively described plasma composition, deposition rate, and film properties. Seman et al. in 2003 [8] showed that ion bombardment had a profound impact on film density and electrochromic performance. More recently, Seman et al. in 2004 [9] reported that diffusion coefficients of H^+ and Li^+ ion intercalated into tungsten oxide films prepared by PECVD were about an order of magnitude greater than those produced by physical vapor deposition (PVD) techniques such as evaporation and sputtering. However, electrochromic WO_xC_y films deposited on flexible PET/ITO substrates by PECVD have not yet been investigated. This study attempts to use low temperature (23 °C) PECVD process with a precursor TC and air, to deposit electrochromic WO_xC_y films onto flexible PET/ITO substrates.

2. Experimental details

A PET/ITO substrate (60 Ω/square, 125 µm thick, 3 cm × 6 cm) was mounted onto the cathode electrode (31 cm radius) plate. Ar gas (99.9% pure) of 4 sccm-carrying TC vapor (the tank and the gas line heated at 110 °C) of 4 sccm and air (99.9% pure) gas of 8.9 sccm were fed into the plasma chamber. Other plasma parameters were set at 12 Pa for chamber pressure, 200 W for power and 8 min for duration.

Field emitted scanning microscopy (FESEM) was used to observe the surface morphology of the PET/ITO/WO_xC_y (the top surface) and to determine the thickness of WO_xC_y films (the cross section). The thickness and deposition rate were found to be 531 nm and 66.4 nm/min. FESEM was collected on a HITACHI S-4800 with an electrical voltage of 1 kV and an electrical current of 5 µA. Data was recorded for a scan area of 500 nm and pixels of 1024 × 840.

Grain boundary fraction (%) on the surface of each sample was calculated by dividing the area of grain boundary to the total area of coatings on the FESEM images using the software of Image-Pro Plus-Version 4.5.0.29 (purchased from Media Cybernetics, Inc.).

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Compositional analyses of samples were performed by a Thermo VG Scientific-Sigma Probe and the system was equipped with an Al Kα X-ray source at 1486.6 eV, with pass energy at 50 eV and charge compensation at 0.4 mA. X-ray photoelectron spectroscopy (XPS) data was recorded at a 53° collecting angle while high resolution spectra had a spot size of 400 μm and analysis depths of ~5 nm. The following binding energies for WO_xC_y coatings were analyzed: $W^{6+}_{4f7/2}$ and $W^{6+}_{4f5/2}$ at 35.1 eV and 37.2 eV; and $W^{5+}_{4f7/2}$ and $W^{5+}_{4f5/2}$ at 33.9 eV and 36.4 eV.

A Jiehan 5000 electrochemical station was used for cyclic voltammetric measurements. The PET/ITO/WO_xC_y was mounted on a working electrode. A Pt grid was used as a counter electrode. The electrolyte was a 0.1 M $LiClO_4$-PC solution. Cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV/s, between −1 and 1 V versus the reference electrode, which was a saturated calomel electrode (SCE) $Hg/Hg_2Cl_2/KCl$ (saturated in water). A glass cell filled with the electrolyte and containing the Pt grid was taken as the background. A Labguide DH2000-BAL spectrophotometer was used to measure the transmittance of PET/ITO/WO_xC_y. The electrochromic performance of the PET/ITO/WO_xC_y was determined in terms of transmittance variation (ΔT), optical density change (ΔOD) and color efficiency (η), which can be determined by Eqs. (2), (3) and (4):

$$\Delta T(\%) = T_{\text{bleached}}(\%) - T_{\text{colored}}(\%) \tag{2}$$

$$\Delta OD = \log\left[\frac{T_{\text{bleached}}(\%)}{T_{\text{colored}}(\%)}\right] \tag{3}$$

$$\eta = \frac{\Delta OD}{q} \tag{4}$$

where $T_{\text{bleached}}(\%)$ and $T_{\text{colored}}(\%)$are the transmittance of the samples in the bleached state (ion intercalation state) and colored state (ion de-intercalation state), and q is the charge intercalation/de-intercalation per unit area.

The quantities x_i and x_d are termed as the intercalation coefficient and de-intercalation coefficient of Li^+ ions. x_i and x_d can be calculated by Eqs. (5), (6) and (7):

$$x_i; x_d = \frac{M_{Li^+}}{M_{WO_xC_y}} \tag{5}$$

$$M_{Li^+} = \frac{\left(q/q_{e^-}\right)}{N} \tag{6}$$

$$M_{WO_xC_y} = \frac{V \times D}{m} \tag{7}$$

where M_{Li^+} is the moles of Li^+ intercalated (de-intercalated), $M_{WO_xC_y}$ is the moles of WO_xC_y film, V is the film volume, D is the film density, m is the atomic weight of WO_xC_y, q is the charge of Li^+ intercalated (de-intercalated), q_{e^-} is the charge of electron intercalated (de-intercalated) and N is Avogadro's number.

3. Results and discussion

3.1. Surface morphology and electrochromic performance

Electrochromic performance of PET/ITO/WO_xC_y is highly affected by its surface properties since Li^+ intercalation and de-intercalation occur on the surface before it sinks deeper in the film. FESEM image in Fig. 1b shows that a porous WO_xC_y film was deposited onto a PET/ITO substrate (see Fig. 1a). Grain boundary fraction of PET/ITO/WO_xC_y at 24.1% allows Li^+ to be easily intercalated and de-intercalated.

Fig. 2 shows the reversible CVs of PET/ITO/WO_xC_y for Li^+ ion intercalation and de-intercalation for 1, 50, 100 and 150 cycles. For 1 cycle of Li^+ ion intercalation and de-intercalation, the cathodic peak current density i_{pc} and anodic peak current density were 0.61 mA/cm^2 and 0.44 mA/cm^2, as shown in Table 1, respectively. The diffusion

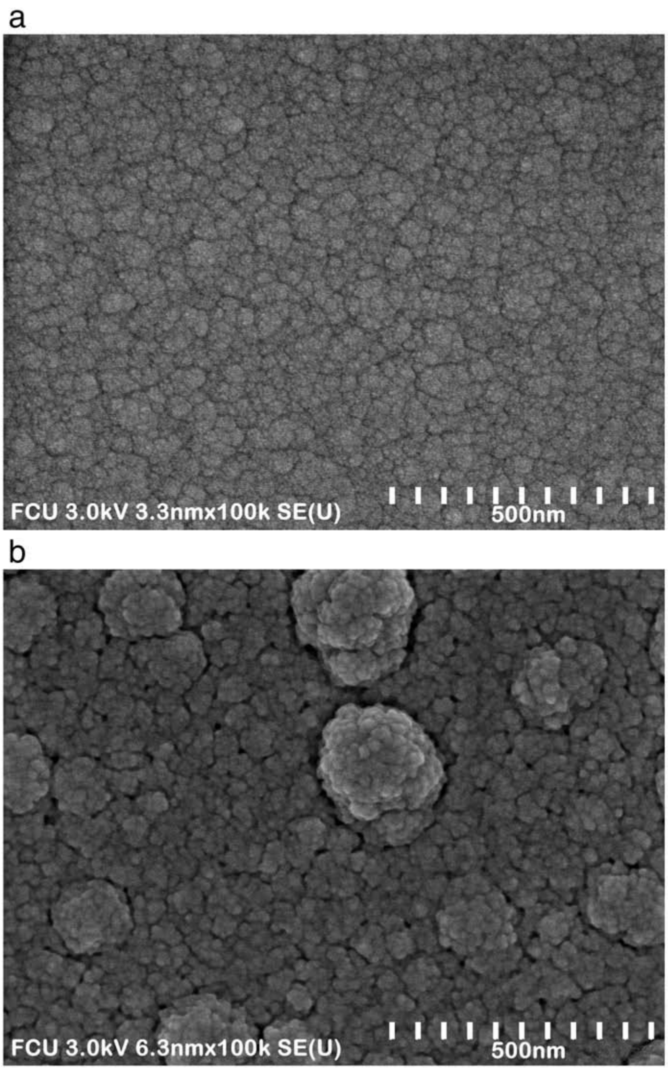

Fig. 1. FESEM images of (a) PET/ITO and (b) PET/ITO/WO_xC_y.

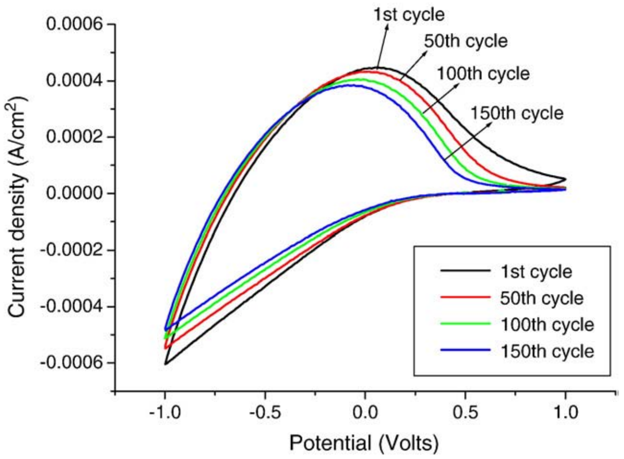

Fig. 2. Cyclic voltammetry of flexible PET/ITO/WO_xC_y for Li^+ ion intercalation and de-intercalation for 1, 50, 100 and 150 cycles.