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Electrochromic characterization of amorphous tungsten oxide films deposited on indium tin oxide and CVD-graphene electrodes by RF magnetron sputtering

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Electrochromism in amorphous tungsten oxide films, lasting and reversible color change to dark blue, is up to injection or withdrawal of electrons. Indium tin oxide (ITO) is widely used as the transparent electrodes for electrochromic devices. We sputtered a-WO_x film on indium tin oxides (ITO) coated flexible polyelthylene terephthalate (PET) substrate. The sheet resistance of ITO/PET is 200 Ohm/sq. To determine optimum condition, we deposited the films under various partial pressures of oxygen and exposure time for adjusting the thickness of the film at room temperature. Optical properties were checked with optical transmittance and Raman spectroscopy of WO_3 film depending on various O_2 pressure. We verified the best condition when WO_3 film was deposited on ITO/PET substrate with 2% O_2 partial pressure and the EC property for graphene /PET application.

Key words: WO_x , Electrochromic, ITO, Graphene, Flexible, Sputtering.

Introduction

Electrochromic (EC) devices at applied voltage are able to change optical properties, reversibly. Because they consume small energy during EC performance, EC devices have attraction in various applications such as smart window, optical displays, and eye wears, etc. [1-3]. Indium tin oxide (ITO) is commonly used as the transparent electrodes. ITO could be utilized to prepare an EC device with a faster response time [4-5]. Graphene is the new potential candidate for transparent conductive electrode to replace ITO due to its superior physical properties [6-12].

EC devices contain an EC film in contact with an electrolyte conducting films as well. The electron conductivity and ion diffusivity in the coloration EC film is an important factor in EC performance.

$$xLi^{x}+xe^{-}+a-WO_{3-y}\leftrightarrow a-Li_{x}WO_{3-y} \quad (1)$$

WO_3 is well known stable electrochromic materials due to its high coloration efficiency [13-14]. WO_3 and NiO are widely used as the cathodic and anodic EC film, respectively. EC materials are able to sustain reversible their optical properties by electrochemical redox process in EC devices.

The demands for flexible EC devices is on the increase. Therefore, it has been necessary for the optimal deposition condition of EC film applied for the flexible and large-area EC devices.

In this study, we report to deposit EC film on the flexible PET film by sputtering without post heat-annealing and to investigate the effect of the Ar/O_2 ratio and sputtering deposition time on EC properties. WO_x, EC film was deposited using RF magnetron sputtering method and the optical density of transmittance had appreciable influence on the coloration and EC response time by the Ar/O_2 ratio. The characteristic of the flexible EC display, WO_x /ITO/PET has been fabricated and demonstrated. Furthermore, WO_x /graphene/PET flexible EC film has been demonstrated.

Experimental Details

WO_x and NiO films were deposited using 4 inch WO_3 target and NiO target, respectively by RF magnetron sputtering method (CS200, ULVAC). This bottom-up system was supplied the maximum RF power of 500W; 13.56 MHz and could be rotated until 20 rpm to smoothen the film surface. The distance between the target material and the substrate was 10 cm. The target and the substrate were laid on the upper side and the bottom of the chamber, respectively.

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Table 1. Deposition condition of WO_x and NiO on ITO/PET.

Conditions	NiO	WO_x					
Pressure; Ar/O_2 (%)	90/10	100/0	99/1	98/2	97/3	96/4	95/5
Deposited time (min)	10	10	10	20	30	40	50
RF power (W)	150	250					
Working pressure (mTorr)	5						

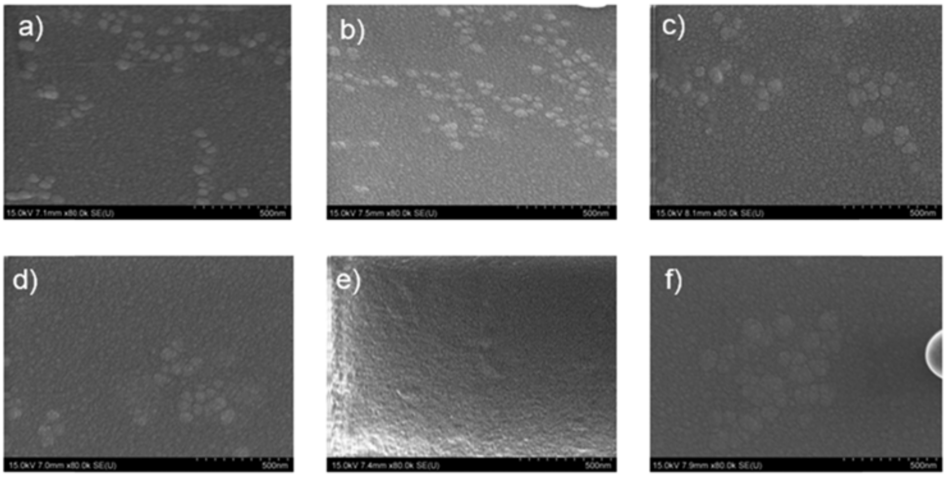

Fig. 1. SEM images of WO_x film with the deposition pressure of Ar/O2 ratio; (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5% of oxygen pressure.

This has advantage that the substrate is free from contamination. The resistivity of prepared ITO/PET film was 200 Ω/. The base pressure was below 5×10^{-7} Torr and the working pressure was 5×10^{-3} Torr for all films examined. The Ar : O_2 percent ratio of pressure was 90 : 10 for NiO deposition and the ratios for WO_x were 99 : 1, 98 : 2, 97 : 3, 96 : 4 and 95 : 5, respectively (Table 1). The pre-sputtering process was performed for 10 min in order to eliminate contaminants from the target. Then sputtering was performed for 10 min at 150 W to be grown NiO film. In the case of WO_x deposition, conducting times are from 10 to 50 min at 250 W. Furthermore, post-annealing was performed at 70 °C for 30min.

WO_x /ITO/PET film and NiO/ITO/PET film were set up at a distance of 1 cm in 1M $LiPF_6$ (in EC/EMC = 1 : 1) solution. The change of coloration in the colored state was observed at applied voltage of -4V.

Scanning electron microscopy (SEM) and Raman spectroscopy (Renishaw spectrometer, wave length: 514 nm) are employed to measure the characteristic of the optimal film. The optical transmittance spectra of EC films were measured in the optical region from 300 to 800 nm using UV-visible-NIR spectrophotometer and the optical contrast value is calculated from transmittance between before and after coloration at d line (wave length $\lambda = 587$ nm). In addition, we used monolayer graphene electrode to verify the potential for substitution from ITO to graphene in the future devices.

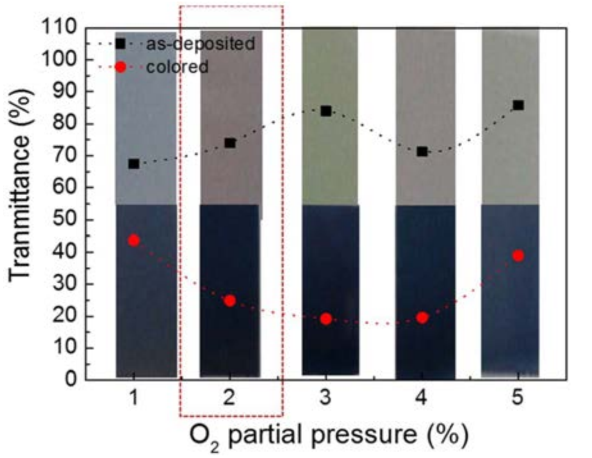

Fig. 2. Differential transmittance and color transition as the deposition pressure; sputtering oxygen partial pressure from 0 to 5% at d line ($\lambda = 587$ nm).

Results and Discussion

Figure 1 shows SEM images of WO_x film deposited with various Ar/O_2 ratios. The surface morphology and roughness of WO_x film were examined. As-deposited WO_x film surface represents in Figure 4(a), (b), (c), (d), (e) and (f) at 0 ~ 5% oxygen pressure, respectively. The top-view SEM images of the films show a continuous and uniform surface of the film. We ascertained the amorphous WO_x film.

The transmittance and color transition between as-deposited and colored WO_x/ITO/PET film can be

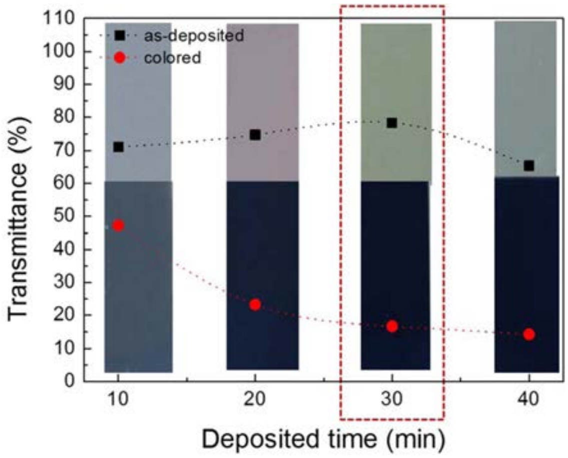

Fig. 3. Differential transmittance and color transition as deposited time from 10 to 40 min at O_2 2% pressure.

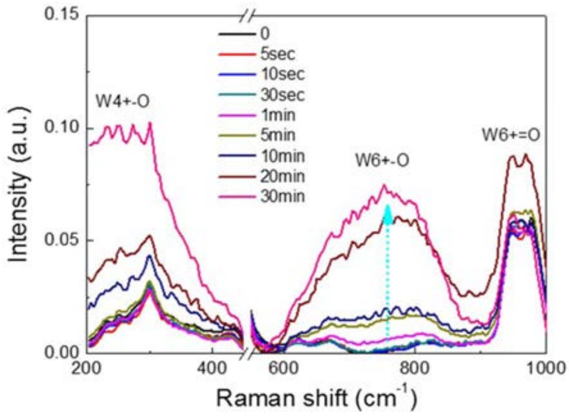

Fig. 4. Raman spectra of WO_x on the deposited time at 2% O_2 pressure; peak related to W^{6+} –O at 770 cm^{-1}, W^{6+} = O at 950 cm^{-1} and W^{4+} –O at 220 cm^{-1}.

shown with increasing partial pressure of oxygen during sputtering process in Figure 2. Difference transmittances are 23.77, 49.17, 64.87, 51.68 and 46.95% at d line (λ = 587 nm), respectively. The optical contrast value is the highest at O_2 3% partial pressure and then it at 2 or 4% are high value, as well. However the reaction time to be colored WO_x /ITO/PET under 2% partial pressure of oxygen was the fastest among them (within 4 sec). Therefore, we selected 2% condition as the optimum oxygen partial pressure.

In order to determine the optimum deposition time of the EC film. WO_x film was grown with the various deposition time from 10 to 40 min at Ar/O_2 = 98/2 pressure. Figure 3 shows the transmittance spectrum and color transition of WO_x /ITO/PET under electric field. The optical contrast value is calculated from the transmittance between as-deposited WO_x film and the colored WO_x film on the ITO/PET. The values are 23.88, 51.41, 61.66, and 51.06% at d line (λ = 587 nm) in deposited for 10, 20, 30 and 40 min, respectively. Figure 4 shows Raman spectra of WO_x depending on

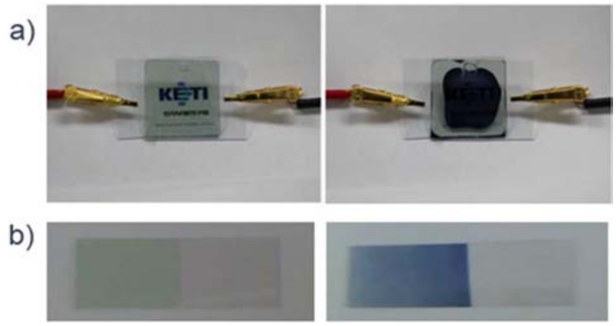

Fig. 5. Photo image of color transition in (a) EC device; WO_x and NiO on ITO/PET and (b) EC film; WO_x on graphene/PET.

various deposited time from 0 to 30 min at Ar/O_2 = 98/2 ratio. The peaks at 770 cm^{-1} , 950 cm^{-1} and 220 cm^{-1} are assigned to the W^{6+} –O, W^{6+} = O and W^{4+} –O, respectively. W^{6+} –O and W^{6+} = O bonds correspond to the crystalline WO_3 and stretching mode of terminal oxygen atoms on the surface cluster, respectively [15-18]. The intensity of the each peak related EC property in WO_x EC film was proportional with deposited time. The film containing W^{4+}–O state has better EC performance due to its oxygen deficiency [14]. The sample deposited for more than 30min was too late to perform coloration. The WO_x film for 30 min at 2% O_2 pressure is expected the optimum condition for EC sample.

Flexible EC device was fabricated by coating an adhesive agent on four sides of the WO_x /ITO/PET film and then NiO/ITO/PET film was laid on the top of the adhesive agent. Liquid electrolyte ($LiPF_6$ in EC/EMC = 1 : 1) was injected between two films, until all air was replaced. Figure 5(a) show the color transition of flexible EC device. In addition, we verified EC property of WO_x/graphene/PET as shown in Figure 5(b). The color transition is from green to dark blue at minus electric filed applied. Graphene is the potential candidate for replacement ITO on EC device.

Conclusions

In summary, we developed electrochromic window deposited WOx and NiO on flexible ITO/PET using sputter. WOx/ITO/PET was showed electrochromic property without special heat treatment after sputtering. We report on the effect of Ar/O_2 ratios on EC properties, and the deposition time of sputtered tungsten oxides. EC film at Ar/O_2 ratio = 98/2 for 30 min had the highest optical density value. The optimum deposition condition of EC film was proposed at Ar/O_2 ratio = 98/2 for 30 min in SEM images and Raman spectra.

Furthermore, the flexible EC device was fabricated based ITO/PET with the optimum WO_x film and identified coloration property. We also verified the electrochromic property of WO_x/graphene/PET, which is suggestive of its potential for flexible EC device applications.

Acknowledgments

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