CONTROLLING THE PACKING DENSITY OF SPUTTERED WO_3 THIN FILMS FOR ELECTROCHROMIC APPLICATIONS

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Received 27 December 2016; Revised 25 March 2017; Accepted 5 April 2017

ABSTRACT

Tungsten oxide (WO_3) thin films were prepared on unheated silicon wafer, glass slide and ITO/glass substrates by pulsed dc reactive magnetron sputtering system. The WO_3 thin films were prepared under various operating pressure from 3−20 mTorr which are controlled by a gate valve of pressure control. The influence of operating pressure on structure, packing density, optical and electrochromic properties of the films were investigated. The results show that all prepared WO_3 thin films are amorphous phase, suggested by X-ray diffraction (XRD) technique. We found that the deposition rate of the WO_3 films is depended on the operating pressure, in which the rate is decreased when the operating pressure is increased. The optical properties and packing density of the WO_3 films were determined by spectroscopic ellipsometry (SE). The results revealed that the WO_3 films deposited at lower operating pressure have higher packing density, comparing with that of higher operating pressure. Finally, the electrochromic property of the films was analysed by measuring the optical transmission changed between colored and bleached states of the WO_3 thin films; the results indicate that the excellent electrochromic property was strongly dependent on the film packing density.

KEYWORDS: *WO_3; Magnetron sputtering; Electrochromic; Spectroscopic ellipsometer*

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INTRODUCTION

The smart window is the innovation of energy saving device. This active device consistes of a multilayer of electrochemical cells which is able to change their optical transmittance reversibly, when low electric field is applied. Indeed, the performance of this device is dependent on the structural composition and configuration of electrochromic device (EC). One novel electrochromic materials widely studied at the moment is tungsten oxide (WO_3). In brief, it is ceramic material in the group of transition elements which has electrons filled in d-orbital; thus when the electrons and ions were injected into the perovskite WO_3 structure, the Fermi energy level is moved upward, so that the optical properties of WO_3 are changed from transparent to colour film, as the chemical reaction is shown in Eq. 1:

$$WO_3 + xM^+ + xe^- \leftrightarrow M_xWO_{3-y} \quad (1)$$

where M^+ is H^+, Li^+, Na^+, or K^+ ions, inserting into WO_3 structure. The M_xWO_{3-y} is the film that has prussian blue color. Therefore, the phenomenon of elctrochromic has the critical factors are consisted of electrochromic materials, electronic properties and ionic diffusivity for preparing electrochromic devices. Indeed, the kinetic propagation of electron and ions are limited by morphology, microstructure and crystallinity of the meterial. The various deposition techniques were used to prepare, and to study the morphology or stoichiometry composition of the WO_3 films. In fact, the conventional deposition methods used to preparing the WO_3 thin films are sputtering with the power supply of direct current (dc), radio frequency (rf) or reactive magnetron sputtering [1], electron beam evaporation [2], sol-gel method [3], electrodeposition [4] and hydrothermal method

[5]. In 2010, X. Sun and his coworker [6] used the reactive dc pulsed magnetron sputtering to study the film density; they found that when the working pressure is high and lower density was occurred, the electrochromic response is faster. Therefore, in this research, the reactive dc pulsed magnetron sputtering was applied to prepare the WO_3 films in which the operating pressure was varied. The pressure was controlled by gauge valve which is installed between the main chamber and turbomolecular pump; in fact, this technique is different from that of X. Sun group. Then, the porousity of the film deposited was analysed by spectroscopic ellipsometer. Moreover, the morphology and crystallinity of the WO_3 films were characterized by field emission secondary electron microscopy (FESEM) and X-ray diffraction (XRD), respectively.

MATERIALS AND METHODS

The tungsten oxide films were deposited by pulsed dc reactive magnetron sputtering. The purity 99.99% of tungsten metal (W) with diameter size of 2 inch was used as the target. Various materials - glass, ITO coated on glass (20 Ω/sq) and bare silicon wafer - were used as the substrates. The vacuum chamber was evacuated (down to 2×10^{-6} Torr base pressure) using turbo molecular pump. During the deposition, the total pressure or operating pressure was controlled by pressure control plate value; here, the pressure was varied from 5 to 20 sccm with 5 sccm increment step (i.e. 4 experiments with operating pressure of 5, 10, 15 and 20 sccm) to study the effect of operating pressure to the properties of the films. The sputtering power was fixed at 150 W for all deposition conditions. The argon and oxygen flow rate are 15 sccm and 7 sccm, respectively. The thickness of WO_3 films were controlled at 300 ± 20 nm. The film structural was studied by X-ray diffraction (XRD; CuK_α: λ = 1.5418 angstrom) while the morphological properties were characterized by field emission secondary electron microscopy (FESEM). Moreover, the electrochromic measurements were performed by cyclic voltmeter (CV) with the potentiostat. The sulfuric acid concentration 0.01 M was used as the electrolyte. CV measurements were applied the voltage in the range from −1.5 to 1.5 V with the 20 mV/s scaning rate. The transmission at coloring and bleaching states of the film was measured by UV-Vis-NIR spectrophotometer in the wavelength range from 350 to 2000 nm.

RESULTS AND DISCUSSION

The structure of WO_3 thin films prepared at various operating pressures characterised by X-ray diffraction technique was shown in Fig. 1a. It is clear that the WO_3 films are amorphous phase, indicating that the sputtering conditions did not provide enough energy to move and rearrange WO_3 atoms, in order to create crystal structure. The optical transmission spectra of the film were shown in Fig. 1b; obviously, the spectra indicate that the transmission increases as the operating pressure increases.

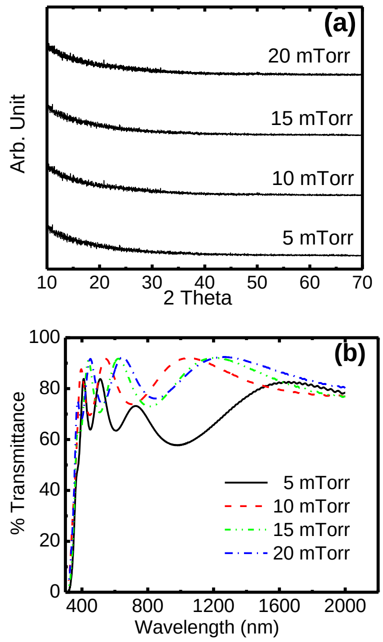


Fig. 1 The WO_3 thin films were deposited (a) XRD pattern of WO_3 films grown on silicon wafer and (b) the transmittance of WO_3 films was grown on glass with various operating pressure.

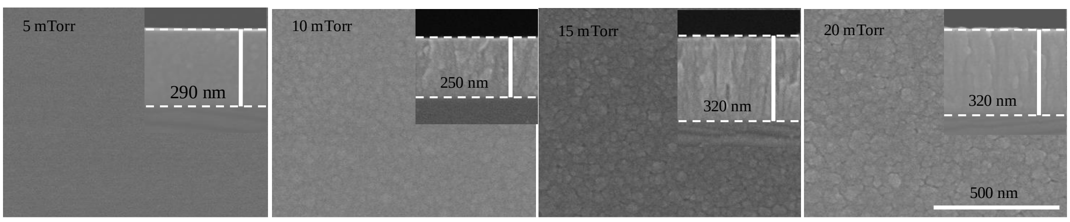


Fig. 2 SEM images of top surface and cross section of WO_3 with various operating pressure

The microstructure and thickness of the films were characterized by FESEM (Fig. 2); it was found that the thickness of the films are around 300 nm (see inset figures). Moreover, we also found that at high operating pressure, the spaces in the film are likely to appear (i.e. at 15 and 20 mTorr). To characterise the porosity of the film, the spectroscopic ellipsometry technique (SE) is used. In brief, the ellipsometer is the instrument which measures the polarisation stated changed - represented as an amplitude ratio, Ψ, and the phase difference, Δ - between the incident- and refleted-polarized light ; the measured Ψ and Δ data could be used to extract the refractive index of the film. Here, we used the ellipsometric data to calculate the refractive index of the films at 550 nm, and then, used the Lorentz-Lorentz relationship (Eq.2) for calculating the porosity (P) of the films [7]. The Lorentz-Lorentz relationship is defined as:

$$P = \left(\frac{n_f^2 - 1}{n_f^2 + 1}\right)\left(\frac{n_b^2 + 1}{n_b^2 - 1}\right) \qquad (2)$$

where f and b subscripts are refer to film and bulk, and n is the refractive index at 550 nm. The refractive index of bulk WO_3 at 550 nm is 2.5 [7]. The comparisons for the effect of operating pressure on refractive index and porosity was plotted in Fig. 3.

The results in Fig. 3 show that the refractive index was decreased and the porosity was increased as operating pressure is increased. These suggest that the WO_3 films are likely to have lower packing density when the operating pressure is higher since the energy per atom is decreased. This energy could also affect the WO_3 film formation clearly seen in FESEM images (Fig. 2): the appearance of space or porosity in the films at high operating pressure.

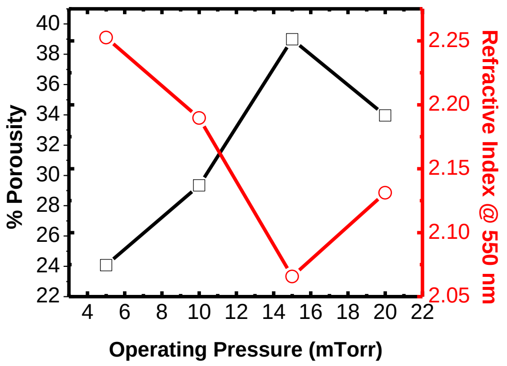


Fig. 3 The effect of operating pressure on refractive index and porosity of WO_3 films.

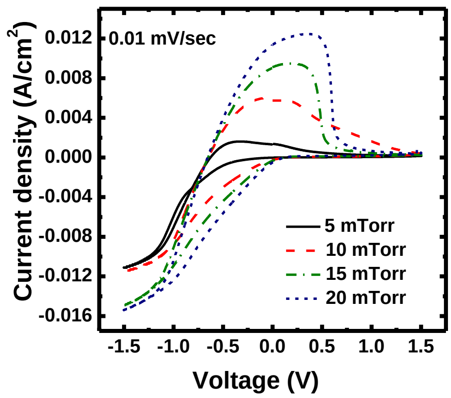
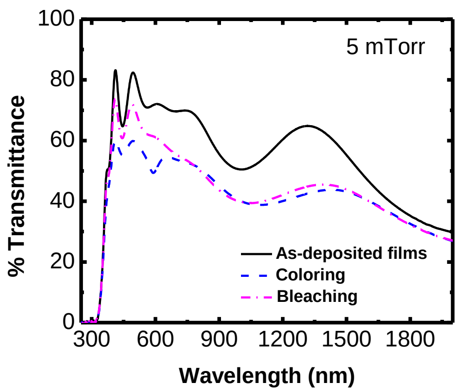


Fig. 4 Cyclic voltammograms of WO_3 films deposited at different operating pressure.

To perform the electrochromic measurements, the WO_3 films were colored and bleached using cyclic voltmeter. The electrical potential varied from −1.5 to +1.5 V with the scanning rate of 0.01 V/sec was applied to the electrochemical cell which had the WO_3 thin films as the working electrode. The CV graph was plotted in Fig. 4; clearly, the coloration efficiency at 20 mTorr operating pressure is higher than that of the others. In fact, this implies that the packing density has the effect on the charge intercalation into the film; the enhancement of ion conductivity could provide by the highly porous film which has a large interface for ion insertion.

Furthermore, the UV-visible-NIR spectroscopy was used to measure the optical transmission of the colored and bleached states of the films (Fig. 5). The results suggest that if the films have high porosity, the ions could insert into the film easier, comparing to that of the dense film. In fact, the highly porous WO3 film deposited at 20 mTorr shows the dark prussian blue colour so that does not permit the almost visible light to pass through it.



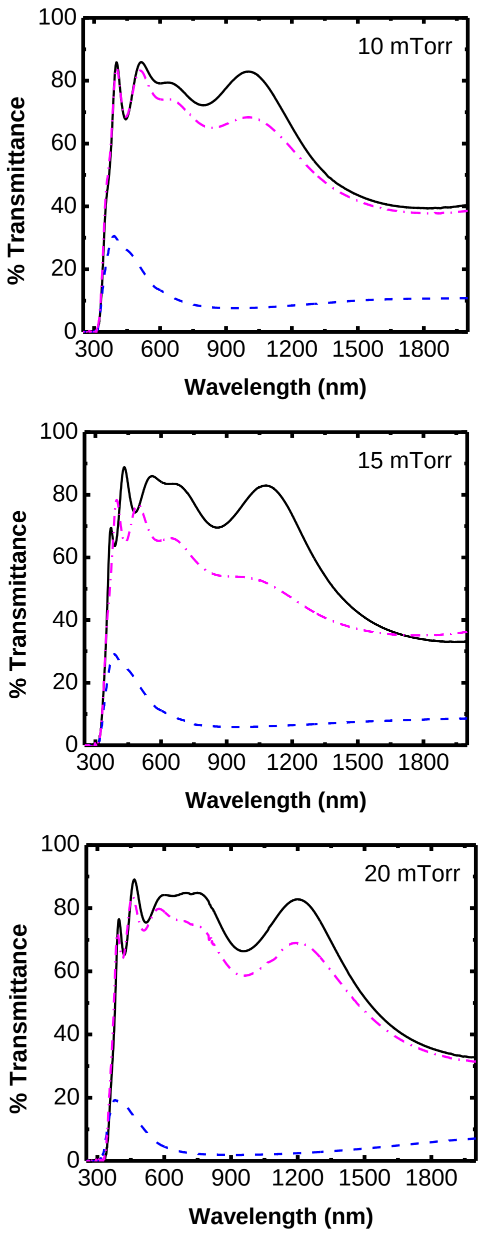


Fig. 5 The transmission spectrum of coloring and bleaching state of WO_3 films which deposited with various operating pressure.

CONCLUSION

The WO_3 thin films were prepared by reactive magnetron sputtering with pulsed dc power supply at various operating pressures. The results show the effect of operating pressure on the microstructure, optical and electrochromic properties of the films. All of the films in this research are amorphous phase. The WO_3 films deposited at high operating pressure are likely to form with high porosity. We suggest that the porosity of the films help to enhance the ion insertion process and so results in enhancing the coloration dynamical process. Furthermore, we also show that the film density affected on the electrochromic properties of the films. This research indicates that the electrochromic property of the film with lower density is better than the film with high density.

ACKNOWLEDGEMENTS

The author appreciate the financial support provided by Srinakharinwirot University and the Faculty of Science, Srinakharinwirot University. We also would like to thank the National Science and Technology for supporting the sputtering system.

REFERENCES

[1] A. Monteiro, M.F. Costa, B. Almeida, V. Teixeira, J. Gago, E. Roman, Structural and optical characterization of WO_3 deposited on glass and ITO, Vacuum. 64 (2002) 287–291.

[2] R. Sivakumar, R. Gopalakrishnan , M. Jayachandran, C. Sanjeeviraja, Preparation and characterization of electron beam evaporated WO_3 thin films, Opt. Mater. 29 (2007) 679–687.

[3] K. Galatsis, Y.X. Li, W. Wlodarski, K. Kalanta-zadeh, Sol-gel prepared MoO_3-WO_3 thin films for O_2 gas sensing, Sensor. Atuator. B. 77 (2001) 478–483.

[4] W. Wang, Y. Ji, H. Xu, H. Li, T. Visan F. Golgovici, A high packing density micro-thermoelectric power generator based on film thermoelectric materials fabricated by electrodeposition technology, Surf. Coat. Tech. 231 (2013) 583–589.

[5] C.S. Wu, Hydrothermal Fabrication of WO_3 Hierarchical Architectures: Structure, Growth and Response, Nanomaterials. 5 (2015) 1250–1255.

[6] X. Sun, Z. Liu, H. Cao, Effect of film density on electrochromic tungsten oxide thin films deposited by reactive dc-pulsed magnetron sputtering, J. Alloys Compd. 5045 (2010) 5418–5421.

[7] Y. Liu, P.H. Daum, Relationship of refractive index to mass density and self-consistency of mixing rules for multicomponent mixtures like ambient aerosols, Aerosol Sci. 39 (2008) 974 – 986.