SYNTHESIS AND INVESTIGATION SOME PROPERTIES OF WO$_3$ ELECTROCHROMIC THIN FILMS

Nguyen Duy Thien*, Vu Dang Tuan, Nguyen Quang Hoa, Sai Cong Doanh, Le Van Vu

Centre for Materials Science, Faculty of Physics, VNU - Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

*Email: duythien_303@yahoo.com

Received: 28 August 2015; Accepted for publication: 28 October 2015

ABSTRACT

The study of electrochromic thin films, which are transparent in the visible range, is significantly important in producing smart doors production and saving energy. This paper reports the results of preparing WO$_3$ thin films on glass substrates and ITO substrates by thermal vacuum evaporation method. The influence of annealing temperature on the properties of thin films was investigated by X-ray diffraction, Raman scattering spectroscopy, X-ray energy dispersive spectroscopy, Atomic force microscopy and absorption and transmittance UV–vis spectroscopy. The results show that WO$_3$ thin films have a high transmittance of about 90% in the visible wavelength from 400 to 900 nm, good substrate adhesion. The WO$_3$ thin films were crystallized at 400 °C and the crystallization of thin films on the ITO substrate better than glass substrate. Electrochromic characteristics of WO$_3$ thin films were investigated by Autolab electrochemical system. The results show the transmittance of WO$_3$ thin film was reduced to around 12% in visible region when increasing the applied voltage from -0.1 V to -0.7 V. The transmittance of the film was completely recovered by using an applied voltage of 2 V.

Keywords: electro-chromic property, electrochemical, WO$_3$, thin film, thermal evaporation.

1. INTRODUCTION

WO$_3$ is a typical materials of the transition metal oxide family, which has been studied quite early [1, 2] because of many interesting physical properties, such as opto-chromic properties [3], electro-chromic properties [4, 5, 6], gas-chromic properties and gas-sensitive properties [7, 8]. These properties make them promising candidates for practical applications. One of such interesting applications of WO$_3$ is to make smart windows, which can adjust light intensity by using a voltage. These high-tech products are very promising and practical for saving energy in the near future.

In recent literature, WO$_3$ thin films have been prepared using various methods such as electron beam deposition [1, 2], vacuum thermal evaporation [3, 9], pulsed laser deposition (PLD) [7] and sputtering [4, 5, 10] technique. In this report, we succeed in fabricating WO$_3$ thin film by vacuum thermal evaporation on glass and ITO substrates. The advantages of this method are simple operation, ease of fabrication of compound thin films, similar thin film composition
Synthesis and investigation some properties of WO$_3$ electrochromic thin films

to source material. Beside, technical parameters could be precisely controlled, to give thin film of high quality.

In this report, it is noted that we had studied the influence of annealing temperature on the crystallization of the films prepared on glass substrates and ITO substrates. The most interesting obtained result is that variation of annealing temperature leads to the formation and competition between crystalline phases of WO$_3$, which in turn result in the changing of optical properties of the film. This phenomenon was observed on XRD patterns and SEM images. We also investigated the electro-chromic properties for further study aiming to applications in smart windows.

2. MATERIALS AND METHODS

WO$_3$ films were fabricated by vacuum thermal evaporation method on Univex 300 system (Leybold, Germany) from bulk WO$_3$ 99.9 % (Merck). Firstly, 2 cm × 2 cm glass substrate (China) and ITO (France) were cleaned by ultrasonic waves in water, ethanol and iso – propanol one after another, then they are dried at 100 °C, the duration of each step is 10 minutes. Finally, the thin films were deposited without using substrate temperature. The pressure inside the chamber was controlled at 7 × 10$^{-4}$ Torr, The distance from the target to the substrate is fixed at 15 cm. The current is 30 A and time was varied from 30 to 150 s, the products were annealed in air at different temperatures in 5 h.

Crystal structure of the thin films was analyzed by using an X-ray diffractometer SIEMENS D5005, Bruker, Germany with a scanning step of 0.03° in the diffraction angle range 2θ from 10° to 70°, and with Cu-K$_\alpha$ ($\lambda = 0.154056$ nm) irradiation. The surface morphology of the samples was observed by using a Nova NANO-SEM-450, FEI electron microscope and atomic force microscopy. The thickness of the thin films was obtained by Dektak 150 VECCO, USA. The UV-vis Transmission spectra were collected by a Shimadzu UV 2450 PC spectrometer. Raman measurements were carried out by using LabRam HR800, Horiba spectrometer with 632.8 nm excitation.

Electro-chromatic characteristics of WO$_3$ thin films were investigated by 302N Autolab electro-chemical system. in which the working electrode (WE) is WO$_3$/ITO, reference electrode (RE) is AgCl, counter electrode (CE) is Pt, the distance between CE and WE is 1cm. Transmittances of coloration and bleaching states were obtained by a Shimadzu UV 2450 PC spectrometer and electro-chromatic efficiency are given by the following formula [12]:

$$\eta = \frac{\Delta OD}{Q} = \frac{1}{Q} \ln \left( \frac{T_b}{T_c} \right)$$

where Q is the amount of charge of the colored states, $T_b$ is transmittances of bleaching states; $T_c$ is transmittances of coloration states.

3. RESULTS AND DISCUSSION

XRD patterns of WO$_3$ thin films on glass annealed in air at various temperatures are presented in Fig. 1A. The results show that thin films annealed at 300 °C is not crystallized, but at 400 °C they have been crystallized. The main phase is triclinic structure with the strongest peaks at 24.2°, corresponding to diffraction from (200) planes. The pattern match well with the standard values (JCPDS card No. 20-1323). Besides, there is a small amount of hexagonal phases (JCPDS card No. 33-1387). WO$_3$ thin films annealed at 500 °C also has two phases as
the last sample but hexagonal phase significantly increased with the strongest peak at 2θ values of 28.4°, corresponding to diffraction from (200) planes, (JCPDS card No. 33-1387). Similar results were observed for WO₃ thin films fabricated on ITO substrate and presented in Fig. 1B. The results show that thin films annealed at 400 °C and 500 °C have crystallized in triclinic phase (JCPDS card No. 20-1323). Thus, the crystallization of the WO₃ thin films fabricated on ITO substrate is better than on glass substrate.

![XRD pattern of WO₃ thin films on glass (A) and ITO substrates (B) annealed at different temperatures.](image)

*Figure 1. XRD pattern of WO₃ thin films on glass (A) and ITO substrates (B) annealed at different temperatures.*

![SEM images](image)

*Figure 2. SEM images of WO₃ thin films on glass was annealed at 400 °C (A), 500 °C (B). AFM images of WO₃ thin films on glass was annealed at 400 °C (C).*

SEM images of WO₃ thin films on glass substrates presented in Figure 2 shows clearly the difference in the morphology of triclinic phase and hexagonal phase. One can see crevices and clear crystal border on the surface of the film. SEM image shown that WO₃ thin film tend to form separate clusters of particles. In particular, the film annealed at 500 °C (Fig. 2B) shows clearly the separation of these two phases. Surface of film exist large crystals of rod shape (5 µm of length, 500 nm of wide) and small particle clusters distributed between rods. We assumes that the rods belong to hexagonal phase while the particle clusters crystallize in triclinic phase.

SEM image combined with XRD analysis results suggest that the crystal rod may grow along the [200] direction of the hexagonal phase. For thin film annealed at 400 °C, of which the main phase is triclinic structure, we observed only one form of particles. However, for thin film
annealed at 500 °C, the amount of triclinic phase is comparable with that of hexagonal phase, we observed two form of particles, corresponding to triclinic phase and hexagonal phase. AFM images of the film annealed at 400 °C shown that the film is quite smooth, with surface roughness of only 2 nm.

![Figure 3](image-url) **Figure 3.** Typical Raman scattering spectra of WO₃ thin films on a glass and ITO substrate annealed at 400 °C, 500 °C (A), and UV-vis Transmission spectra of WO₃ thin films on a glass substrate annealed at different temperatures (B).

The typical Raman scattering spectra of WO₃ thin films are presented in Fig. 3A. The results shown that Raman scattering spectra of WO₃ thin films on a glass and ITO substrate annealed at 400 °C, 500 °C exhibit five Raman modes at around 130 cm⁻¹, 270 cm⁻¹, 323 cm⁻¹, 712 cm⁻¹ and 806 cm⁻¹. The scattering peaks around 270 cm⁻¹ and 323 cm⁻¹ are assigned to the bending vibration δ(O-W-O). The scattering peaks around 713 cm⁻¹ can belongs to the O-W-O mode of WO₃. The strongest peaks at around 806 cm⁻¹ are assigned to stretching vibration v(O-W-O) [11]. The scattering peaks of WO₃ thin films on ITO at wave-number less than 400 cm⁻¹ have low intensity, which can explained by the influence of the ITO substrate to the crystallization of thin films.

Figure 3B is the transmission spectra of thin films WO₃/glass (thickness 550 nm) fabricated in the same conditions after being annealed in air at different temperatures. Before annealing, transmittance of the films is relatively low (about 50%). After being annealed at 200 °C, 300 °C and 400 °C, transmittance increased to about 90%. WO₃ thin films was created in high vacuum, so it is very likely that there exist many vacancies of oxygen in the samples, leading to the formation of W⁴⁺ and W⁵⁺ ions in lattice structure. Such W⁴⁺ and W⁵⁺ ions can act as color center to absorb light strongly in the visible and infrared range. When the annealing temperature was gradually increased, the diffusion of oxygen into the films helps to reduce the number of W⁴⁺ W⁵⁺ ions, therefore, the transmission of the films is improved. It should be noted that the transmittance of the film annealed at 500 °C lower than that of the other films. We suppose that this phenomenon is related to the difference of the crystal structure in these samples.

Electro-chromic characteristics (bleaching and coloration) of WO₃ thin films were presented in Fig. 4. Figure 4A is the transmission spectra of thin film WO₃/ITO (thickness 230 nm) measured before and after applying different negative bias voltages from 0 V to -0.7 V to the working electrode in the duration of 180 s. The results shown that, the initial transmittance at
900 nm of WO$_3$/ITO thin film was about 90% and the transmittance was significantly reduced to only 10% when applying a voltage of -0.7 V. The color of the film changes from transparent to a dark green color, respectively.

Figure 4B is the transmission spectra of thin film after applying positive bias voltage to the working electrode in the same amount of time. We can see a large difference in transmittance spectra at 900 nm of the film in the colored (curve 1) and bleached (curve b) states. Transmittance was about 10% in colored state and was increased to 80%, when a bias voltage was increased from -0.7 V to 2 V. This final state is called bleached state. However, the bleaching processes is not perfect, the film required a higher voltage or longer time to return to its original state.

![Figure 4. The transmission spectra of thin films WO$_3$/ITO: The coloration processes (A) and the bleaching processes (B).](image)

![Figure 5. (A) - Time dependence of the current density of WO$_3$ under a negative bias voltage of -0.7 V, (B) -The transmission spectra of WO$_3$/ITO thin films corresponding to the colored state (at - 0.7 V) and the bleached state (at 1.5 V).](image)

From transmission spectra, one can see that the rate of coloring process is higher than that of the bleaching process. We think that reason of this phenomenon is the infiltration and escape
Synthesis and investigation some properties of WO$_3$ electrochromic thin films

of H$^+$ in the electrolyte solution into lattice structure of the thin films under the effect of electric field. These results are in agreement with some other publications [4, 5, 10]. It is noted that transmittance at 550 nm (the sensitivity wave length of human eye) was greatly reduced from 85 % to 52 %, 45 % and 40 % corresponding to negative bias voltage ranging from 0 V to -0.7V. Vice versa, the transmittance restores from 40 % up to 65 % at 0.3 V and 90 % at 1.5 V.

Figure 5A is the time dependence plot of the current density of WO$_3$ under a negative bias voltage of -0.7 V. We can see that the current density increased fast and reached a saturate value in 30 sec. The amount of charge (Q) is calculated based on the formula:

$$Q = \int_{t_1}^{t_2} j(t)dt$$

for electrochromic efficiency, we investigated the coloring and bleaching during 30 sec corresponding to negative and positive bias voltage of -0.7 V and 1.5 V, and the transmittance spectrum were shown in Figure 5B.

At a wavelength of 550 nm $Q = 8$ mC x cm$^2$, $T_b = 80 %$, $T_c = 67 %$, the estimated coloration efficiency ($\eta$) was 22.2 cm$^2$ x C$^{-1}$. This electro-chromic efficiency is lower than the electro-chromic efficiency of TiO$_2$/WO$_3$ composite thin film in LiClO$_4$ + Propylene Carbonate electrolyte [12] which may be due to the influence of porosity, thickness of the film and the distance between the electrodes. However, it is still better than the data published using similar electrolyte [10].

4. CONCLUSION

WO$_3$ thin films with low surface roughness were successfully fabricated by vacuum thermal evaporation method on glass substrate and ITO substrate. There was a competition between hexagonal phase and triclinic phase in the crystal structure of thin films grown on glass substrates, while films prepared on ITO substrate composed of only triclinic phase. The formation and competition between the crystalline phase were studied and discussed based on both XRD patterns and SEM images. Effects of annealing on the transmittance of the thin films were also investigated. Especially the electro-chromic properties of thin films were studied thoroughly. The results showed that electro-chromic effect is clear in our thin films, the coloring process is faster bleaching process with a coloration efficiency $\eta = 22.2$ cm$^2$ x C$^{-1}$. All of the results are the basis for further studies of electro-chromic properties of WO$_3$ in the field of applications in smart windows.

Acknowledgments. The authors thank the VNU project "Strengthening research and training capacity in field of Nano Science and Technology, and Applications in Medical, Pharmaceutical, Food, Biology, Environmental protection and climate change adaptation in the direction of sustainable development" for having facilitated the equipment to complete this work.

REFERENCES


TÓM TẮT

NGHIÊN CỨU CHẾ TẠO VÀ KHẢO SÁT TÍNH CHẤT CỦA MÀNG MỎNG ĐIỆN SẮC WO₃

Nguyễn Duy Thiện*, Vũ Đăng Tuấn, Nguyễn Quang Hòa, Sai Công Doanh, Lê Văn Vũ

Trung tâm Khoa học vật liệu, Khoa Vật lý, Đại học Khoa học tự nhiên, 334 Nguyễn Trãi, Thanh Xuân, Hà Nội.

*Email: duythien_303@yahoo.com

Nghiên cứu màng mỏng điện sắc trong vùng ánh sáng khả kiến có ý nghĩa quan trọng trong việc sản xuất các cửa kính thông minh và tiết kiệm năng lượng. Báo cáo trình bày các kết quả
nghiên cứu màng mỏng WO3 trên để thủy tinh và để ITO bằng phương pháp bọc bay nhiệt chân không tại nhiệt độ phòng. Ánh hưởng của nhiệt độ ướt lên tính chất của vật liệu đã được khảo sát bằng phổ nhiễu xạ tia X, phổ tán xạ Raman, phổ tán sắc năng lượng, hiện vi lục nguyên tử và phổ hấp thụ, truyền qua UV –vis. Kết quả nhận được cho thấy màng có độ truyền qua cao trong vùng ánh sáng khá kiên, độ bám dính tốt tốt, màng kết tinh tốt ở 400 ºC, màng trên để ITO cho thấy sự kết tinh tốt hơn trên để thủy tinh. Tính chất điện sắc đặc trưng của màng đã được khảo sát bằng hệ điện hóa autolab. Quá trình nhuộm màu cho thấy hệ số truyền qua của màng giảm dần trong dải sóng 400 – 900 nm khi tăng dải hiệu điện thế đạt từ - 0,1V đến - 0,7V. Hệ số truyền qua tại điện thế -0,7V chỉ còn 12 %. Khi đảo chiều điện cực, với hiệu điện thế 2V màng được tẩy trắng hoàn toàn.

Từ khóa: ferrite, thủy nhiệt, đồng kết tủa, NiFe₂O₄.