

Investigation of Electrodeposited WO₃ Film with Heat Treatment

Yih-Min Yeh¹ and Hsiang Chen²

¹WuFeng University

²National Chi Nan University

Received: November 11, 2013, Accepted: December 28, 2013, Available online: February 26, 2014

Abstract: In this research, we propose an alternative method to fabricate WO₃ films as electrochromatic devices (ECDs). To fabricate the electrochromic film, we electrochemically deposit a WO₃ film on FTO (fluorine-doped tin oxide). The deposited film was crystallized with heat treatment at various temperatures. To investigate the material quality of the film in different deposition and heat treatment conditions, X-ray diffraction (XRD) was used to examine the crystalline structure and scanning electron microscope (SEM) was used to analyze the surface morphology. Furthermore, the electrical performance of the film was evaluated by cyclic voltammetry (CV) and the transmittance modulation could still attain above 40% after 1000 times repeated cycles. The electrochromatic behavior has been demonstrated in wavelength between 780 nm to 1050 nm.

Keywords: WO₃, electrodeposition, electrochromatic device, cyclic voltammetry, heat treatment

1. INTRODUCTION

Electrochromism has attracted much attention recently, in part due to its application of light modulation and heat load control. Among traditional electrochromic materials, WO₃ film has emerged to become critically important for electrochromic devices such as smart windows capable of varying the throughput of visible light, and solar energy applications. Since WO₃ film with a perovskite-like structure was first demonstrated by Deb et al. in 1969 [1][2], various preparation methods have been proposed, including vacuum and non-vacuum process fabrication for WO₃ film deposition [3]-[6]. Of these methods non-vacuum fabrication methods offer advantages in terms of low cost, large area fabrication, and good adhesion to the substrate [7][8]. In this study, we present a simple method for depositing the film [9][10]. In contrast to previous studies, we grow high-performance WO₃ film with new recipes for electrochemical deposition. Na₂WO₄ as the tungsten source is mixed to H₂O₂ prior to being acidified with sulfuric acid. Various concentrations of sulfuric acid were added to adjust the pH values of the solution. Then, amorphous electrodeposited films were processed with heat-treated WO₃ films. A well-crystallized film with superior characteristics was formed after heat treatment at an optimal temperature. To examine the final film quality, struc-

tural properties were characterized, and electrical and optical analyses were performed to evaluate film performance. Our findings indicate that a temperature of 400°C is the optimum heat treatment condition.

2. EXPERIMENTAL

To fabricate the electrochromic film, we deposited a WO₃ film on FTO (fluorine-doped tin oxide) as the work electrode with an area of 2 cm × 1.5 cm. The plating solution was made up by the mixture of Lithium perchlorate and LiClO propylene carbonate. The electrolyte compositions were Na₂WO₄, H₂O₂, and H₂SO₄. During the deposition process, the system use constant voltage to electrodeposit the WO₃ film for 30 minutes with an AUTOLAB potentiostat/galvanostat model PGSTAT320 power supply unit. The pH values of the solution were controlled at 1.1, 1.5, and 1.9 by adding different concentrations of sulfuric acid to find a proper deposition voltage, and the film was deposited at room temperature at 1.6, 1.7, 1.8 and 1.9 V via a saturated calomel electrode (SCE). After electrodeposition was done, the film was processed with heat treatment to for crystallization. The temperature rate during the heat treatment was 10°C per minute, and the final temperature of heat elevation varied from 100°C to 400°C. SEM, XRD, cyclic voltammetry and transmittance measurements were applied to evaluate the film quality under different deposition voltages and heat treatment conditions.

*To whom correspondence should be addressed: Email:
Phone:

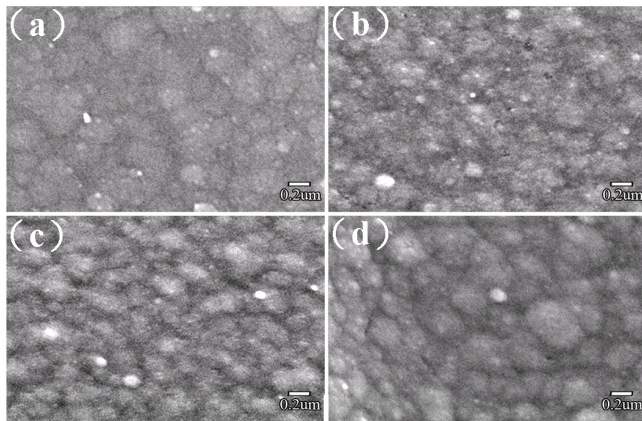


Figure 1. SEM images of surface morphology with various biased voltages of (a) 1.6 (b) 1.7 (c) 1.8 and (d) 1.9 V.

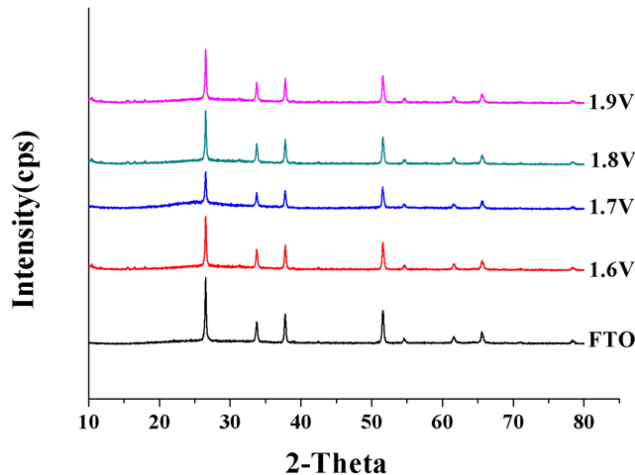


Figure 2. XRD analysis of the deposited film with various biased voltages.

3. RESULTS AND DISCUSSIONS

To evaluate preferable deposition conditions, the WO_3 precursor film was grown under different galvanic deposition voltages in solutions with differing pH values. SEM images and XRD diffraction analyses were applied to examine the film quality in relation to growth conditions. SEM images of surface morphology of the WO_3 film deposited under different voltages are shown in Fig. 1 (a), (b), (c), and (d). Since the deposition rate with an applied voltage below 1.6 V was too slow, deposition voltages from 1.6 V to 1.9 V were chosen. As the deposition voltage increased to 1.8 V or 1.9 V, the grain size increased but the surface became uneven. We therefore selected a deposition voltage of 1.6 V for further investigation. In addition, XRD analysis shown in Fig. 2 reveals that the precursor film was amorphous because the FTO substrate had a better crystallization than the deposited film. As the voltage further increased to 1.8 V or 1.9 V, the high peaks in the XRD analysis signify large grain crystallization on an uneven surface, consistent with the SEM images. Based on the XRD and SEM measurements, we selected to

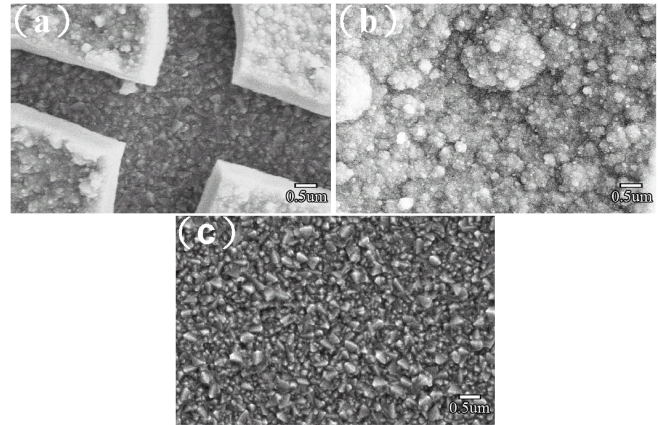


Figure 3. SEM images of surface morphology in solutions with various pH values of (a) 1.1 (b) 1.5 and (c) 1.9.

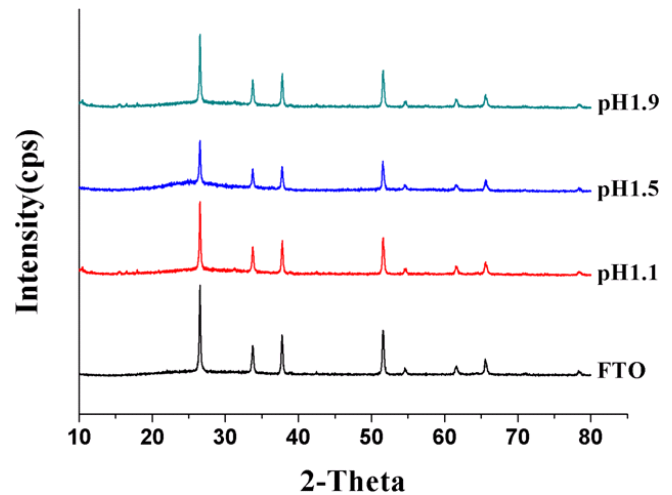


Figure 4. XRD analysis of the deposited film in solutions with various pH values.

deposit the film at 1.6 V to form a flat and compact WO_3 precursor film.

We also explored the influence of the pH values of the solution. The pH values of the plating solution were controlled at 1.1, 1.5, and 1.9 by adding different concentrations of sulfuric acid. Fig. 3(a), (b), and (c) show the deposited film in plating solution with pH values of 1.1, 1.5, and 1.9 at 1.6 V for 30 minutes. As shown in Fig. 3(a), apparent cracks occurred on the surface of the deposited film in the plating solution with a pH value of 1.1. As the pH value in the solution was increased to 1.5, the deposited film became more uniform. Crystallization of the WO_3 precursor film was presented on top of the FTO substrate. When the pH value was further increased to 1.9, the film was unable to grow on top of the FTO substrate. The FTO substrate is presented in the SEM image as shown in Fig. 3(c). In contrast to the SEM images, the XRD analysis as shown in Fig. 4 demonstrates consistent results. For the deposited film in a plating solution with a pH value of 1.1, the XRD pattern shows a cracked FTO substrate pattern. Similarly, the de-

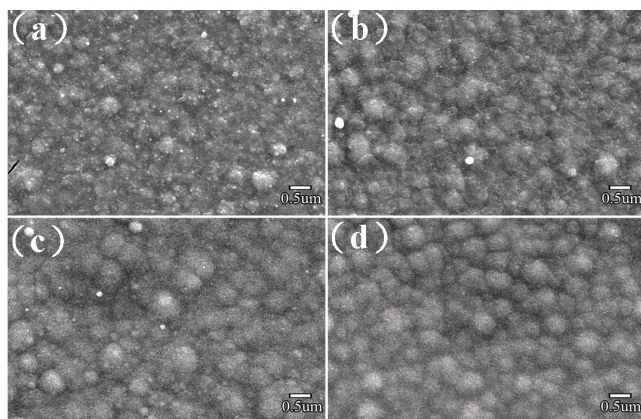


Figure 5. SEM images of surface morphology of the WO₃ precursor sulfured with different final temperatures of (a) 100°C, (b) 200°C, (c) 300°C, and (d) 400°C.

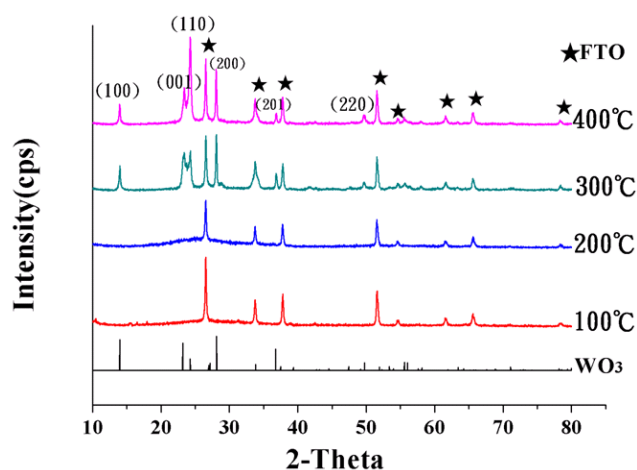


Figure 6. XRD analysis of the WO₃ precursor sulfured with different final temperatures of (a) 100°C, (b) 200°C, (c) 300°C, and (d) 400°C.

posited film in a plating solution with a pH value of 1.9 also resembles the FTO substrate pattern because the substrate was laid bare. Based on the material analyses, a deposition voltage of 1.6 V and a solution with a pH value of 1.5 is optimal for forming high-quality precursor WO₃ film.

After an appropriate deposition condition for the precursor film was determined, the precursor film was processed with heat treatment to enhance crystallization. The heat treatment was performed in a quartz tube with a temperature rate of 10°C per minute and a final temperature from 100°C to 400°C. Since high temperatures near 500°C may damage the FTO substrate, the final temperature was set to 100°C, 200°C, 300°C, and 400°C.

To examine different heat treatment conditions, SEM images of surface morphology of the WO₃ deposited at 1.6 V with different final temperatures are presented in Fig. 5(a), (b), (c) and (d). At lower final temperatures of 100°C, 200°C, and 300°C, the processed film was more amorphous and had many white particles. As

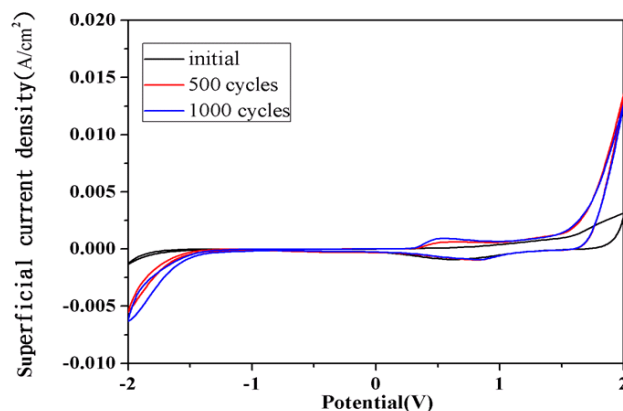


Figure 7. Cyclic voltammetric tests for the deposited film.

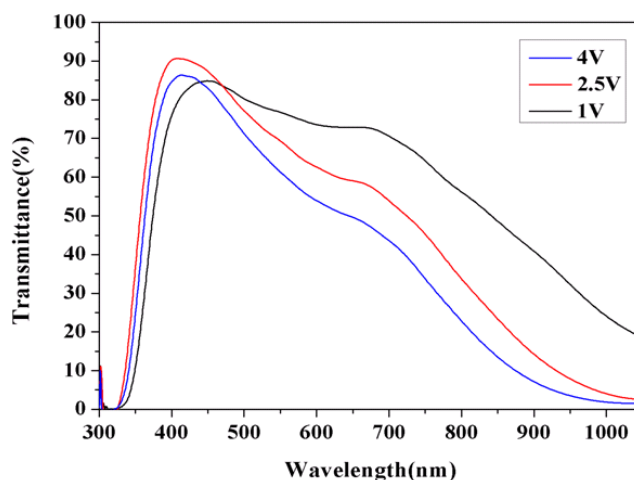


Figure 8. Transmittance from 300 nm to 1100 nm of the film at biased voltages of 1 V, 2.5 V, and 4 V.

the final temperatures were increased from 100°C to 400°C, the WO₃ became better crystallized and many of the small white particles disappeared.

Those white particles should be precursors of well-crystallized WO₃ during phase transition. At high heat treatment temperatures, the precursor particles are fully transformed to a better crystallized film, as shown in Fig. 5(d). The XRD analyses in Fig. 6 present the crystallization phase of the heat-treated WO₃. The crystallization phase of the films with final temperatures of 300°C and 400°C can be clearly observed, confirming the SEM results. The WO₃ film with a higher heat treatment of 400°C presents stronger crystalline phases of WO₃.

We then performed cyclic voltammetric tests for the film deposited at 1.6 V with a final temperature of 400°C for 500 cycles, 1000 cycles and an initial condition from -2 V to 2 V, as shown in Fig. 7. Although the superficial current density decreases after 500 and 1000 cycles, the current density can still reach 10 mA/cm².

Finally, we analyzed optical properties of the film by measuring the transmittance from 300 nm to 1100 nm at biased voltages of 1 V, 2.5 V, and 4 V, as shown in Fig. 8. The transmittance of light

with wavelengths between 300 nm to 400 nm are similar under different biased voltages, while the transmittance of light with wavelengths between 780 nm to 1050 nm decreased drastically as the biased voltage increased from 1 V to 4 V, indicating that WO₃ can effectively shelter light with wavelengths in this range.

4. CONCLUSIONS

Our research has determined that WO₃ electrochromic film is best fabricated at deposition voltage of 1.6 V in a plating solution with a pH value of 1.5 under proper heat treatment conditions. We believe that these findings can further enhance the development of high-quality WO₃ electrochromic film for use in future device applications.

REFERENCES

- [1] K. Bange, *Solar Energy Materials & Solar Cells*, 58, 1 (1999).
- [2] C.G. Granqvist, *Solar Energy Materials & Solar Cells*, 60, 201 (2000).
- [3] G. Leftheriotis, *Solar Energy Materials and Solar Cells*, 83, 115 (2004).
- [4] Julia Khalack, P.V. Ashrit, *Appl. Phys. Lett.*, 89, 211112 (2006).
- [5] S.A. Agnihotry, K.K. Saini, T.K. Saxena, Subhas Chandra, *Thin Solid Films*, 141, 183 (1986).
- [6] B.A. Budkevich, I.A. Ges, S.P. Zhvayyi, G.D. Ivlev, V.A. Pilipovich, *Physica Status Solidi*, 110, 155 (1988).
- [7] Hee-Sang Shim, Hyo-Jin Ahn, Youn-Su Kim, Yung-Eun Sung, and Won Bae Kim, *Journal of Nanoscience and Nanotechnology*, 6, 3572 (2006).
- [8] Z. Yu, X. Jia, J. Du, J. Zhang, *Solar Energy Materials & Solar Cells*, 64, 55 (2000).
- [9] M. Hepel, *J. Chem. Educ.*, 85, 125 (2008).
- [10] M. Ranjbar, N. Tahmasebi Garavand, S.M. Mahdavi, A. Iradjizad, *Solar Energy Materials & Solar Cells*, 94, 201 (2010).