

EFFECT OF ANNEALED AMBIENT ON STRUCTURAL, MORPHOLOGICAL AND ELECTROCHROMIC PROPERTIES OF WO₃ NANOPlates

Sayan Chaiwas¹, Patinya Sakwan¹, Chanunthorn Chananonwathorn², Wantanee Hinceeranun², Mati Horprathum² and Narong Sangwaranatee^{3,*}

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Abstract

In this study, we report the metal oxide nanostructure for electrochromic application based on tungsten oxide (WO₃) material. The WO₃ nanostructure was prepared by three steps: (1) tungsten metallic films were deposited onto ITO coated glass substrate via dc magnetron sputtering. (2) The WO₃ nanostructures were grown on tungsten film by acid treatment process. After acid treatment process, the tungsten oxide hydrate (WO₃•H₂O) with nanostructure was developed. Final step, the tungsten oxide hydrate were annealed at 400°C for 2 h. The effect of annealed ambient on morphology, structural, optical and electrochromic properties was investigated using X-ray diffraction, field emission scanning electron microscopic, transmission electron microscope (TEM) and UV-Vis-NIR spectrophotometer. It was demonstrated that the annealing ambient played an important role in influential the crystal phase, morphology and optical property and of the tungsten oxide hydrate film. The chromogenic mechanism from the thermochromism phenomenon could be found at sample annealed in vacuum ambient. The prepared sample annealed in air ambient depict the electrochromic behavior in H₂SO₄ electrolyte solution.

Keywords: Electrochromic, WO₃, nanoplate, acid treatment

¹ Chitralada Technology College, 604 The Bureau of Royal Household Sanam-Suepa Bangkok 10300, Thailand.

² Optical Thin-Film Laboratory, National Electronics and Computer Technology Center, Pathumthani 12120, Thailand.

³ Applied Physics, Faculty of Science and Technology, Suan Sunandha Rajabhat University, Bangkok 10300, Thailand. E-mail: narong.sa@ssru.ac.th

* Corresponding author

Introduction

From the past decade, the interest in electrochromic (EC) devices has increased due to their application in solar light control and energy saving in smart windows (Tuna *et al.*, 2015). The EC materials can maintain a reversible change in the optical transmittance when electrochemically oxidized or reduced. The EC material include many of the transition metal oxides, such as WO_3 , V_2O_5 , TiO_2 , and NiO have been widely investigated (Papaefthimiou *et al.*, 2001; Cheng *et al.*, 2006; Liu *et al.*, 2009; Tuna *et al.*, 2015; Atak *et al.*, 2017; Wei *et al.*, 2017.). Among these materials, the WO_3 exhibits extensively studied due to their high coloration efficiency, fast response and excellent chemical stability. As we know, the addition of nanostructure WO_3 material such as nanowire (Cai *et al.*, 2001; Lin *et al.*, 2015), nanorod (Ham *et al.*, 2010; Horprathum *et al.*, 2013; Wang *et al.*, 2014; Horprathum *et al.*, 2014) and nanoplate (Su *et al.*, 2010; Ng *et al.*, 2015; Martins Neto *et al.*, 2016) have attracted much attention in the EC performance improvement. Several technique can be applied to fabricate of nanostructure WO_3 such as vapor-liquid-solid (VLS), glancing angle deposition, anodization, hydrothermal and acid treatment. The acid treatment was good candidate because of low temperature process, cost-effective, applicable in large area and promising for flexible substrate.

Generally, as-prepared sample via the acid treatment process was produced tungsten oxide hydrates ($\text{WO}_3 \cdot \text{H}_2\text{O}$). To improve crystallinity, the annealed treatment process was required for phase transformation to monoclinic WO_3 . Here, we investigated the effect of annealed ambient on the structural, morphological and EC properties of nanoplate WO_3 films prepared by dc magnetron sputtering and acid treatment process. The result demonstrated that annealed in air ambient display good EC property which related to the film stoichiometry.

Materials and Methods

The tungsten (W) films were prepared by dc magnetron sputtering deposition by a purity tungsten (99.99%) target with a 2 inch diameter (K.J. Lesker). The silicon wafer (100) and the commercial ITO-coated glass were used as substrates for the structural and EC property measurement, respectively. After a based pressure of 10^{-6} Torr, W target was sputtered in 99.999% argon atmospheres at 10 mTorr and sputtering power 15 W for 10 min. No an internal heating and bias substrate was applied during the film deposition. Subsequently, the W film were immersed in 1.5 M nitric acids (HNO_3) solution for 30 min in order to grown the $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanoplate. Following the acid treatment, the prepared samples were rinsed with DI water and dried in N_2 atmospher. Finally, all prepared samples were annealed at 400°C for 2 h in air, low vacuum (5×10^{-2} mbar) and high vacuum state (8×10^{-6} mbar) ambient.

The phase and crystallinity of the WO_3 nanoplates were characterized by X-ray diffraction with a Rigaku. The morphologies of the samples were investigated with field-emission scanning electron microscope (Hitachi S-5200) and Transmission electron microscope (JEOL). The EC measurements were carried in 0.01 M H_2SO_4 . Note that the EC property were study in 1 cycle of colored and bleached states. The voltage applied between the counter electrode and working electrode was ± 1.5 V using a scanning rate of 0.1mV/s. UV-VIS-NIR spectra were taken as for the deposition specimen colored at -1.5 V and bleached at +1.5 V, respectively using a Agilent, Cary 7,000 spectrometer operated in the wavelength rang of 250-2,000 nm.

Results and Discussion

Figure 1 shows the XRD patterns of the before and after annealed samples at 400°C for 2 hat different ambient. The peaks of as-prepared samples before annealed treatment could be

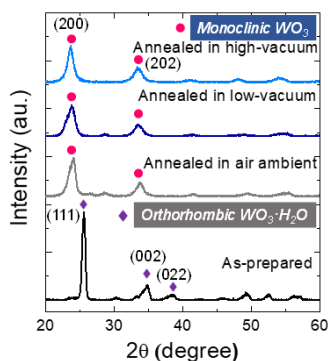


Figure 1. XRD pattern of before and after annealed the prepared samples at different annealed ambient

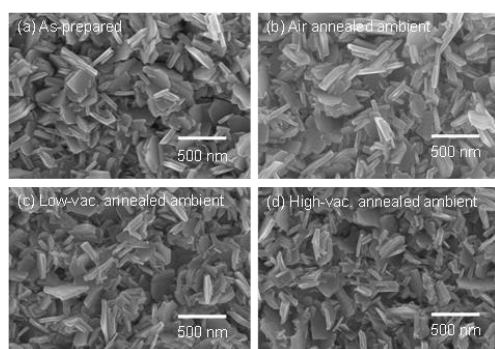


Figure 2. FESEM images of before and after annealed the prepared samples at different annealed ambient

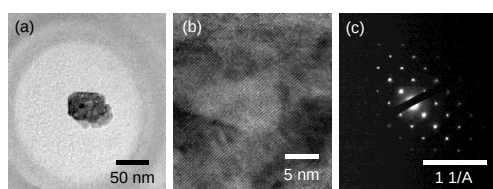


Figure 3. TEM and HRTEM analysis of annealed WO₃ nanoplate at air ambient; (a) morphology, (b) d-spacing and (c) SAED pattern

indexed to the orthorhombic phase of WO₃·H₂O (JCPDS Cards 43-0679). It could be noticed that the prepared sample annealed in air, low and high vacuum stage have shown match well with the monoclinic phase with

progress of (200) and (202) reflections (JCPDS Cards 83-0950).

Figure 2(a)-(d) presents the FE-SEM images for all samples prepared on Si substrate. From the result, we found that rectangular nanoplate cover on the substrate and no other morphologies emerge, indicating a high yield of the nanoplate structure. Moreover, the average width of WO₃ nanoplates with different amounts were calculated to be 324±63, 176±30, 202±48 and 267±58 nm for the as-prepared sample, annealed in air, annealed in low vacuum and annealed in high vacuum, respectively. In addition, the plate thickness not show a significantly change with the annealed ambient. TEM, HRTEM and selected area electron diffraction (SAED) analysis of the annealed WO₃ nanoplate in air ambient have been carried out as shown in Figure 3. The TEM images clearly indicate that the sample was square nanoplate (Figure 3(a)). The fringes observed in HRTEM image with inter-planar spacing of 0.384 nm oriented along the (002) lattice plane of monoclinic WO₃ as shown in Figure 3(b). Figure 3(c) shows corresponding SAED pattern which further ascertains that the sample was single crystalline. The single crystalline WO₃ nanoplate would be of benefit to increased electrochromic property.

Photographs of the prepared sample on ITO coated glass substrate before and after annealed at different ambient were shown in Figure 4. The as-prepared sample after acid treatment without annealed process was yellowish because of the presence of tungsten oxide hydrate (Figure 4(a)). The films annealed in air ambient revealed lighter yellowish color owing to transformation of the monoclinic WO₃ (Figure 4(b)). In addition, the film annealed in low and high vacuum stage was blue and dark blue color, respectively, as the film been colored by chromogenic mechanism due to the thermochromism phenomenon of the heating WO₃ film in vacuum (Goulding *et al.*, 1983). shows the transmission spectra of the annealed WO₃ nanoplates at air ambient under their as-prepared, colored and bleached states in the

wavelength of 250-2000 nm. The results indicated the as-prepared and bleached states had high transmittances, and colored states had low transmittance in visible region. The coloration mechanism in WO_3 can be explained by the inter-valence transition between $\text{W}^{5+} \leftrightarrow \text{W}^{6+}$ when applied the voltage.

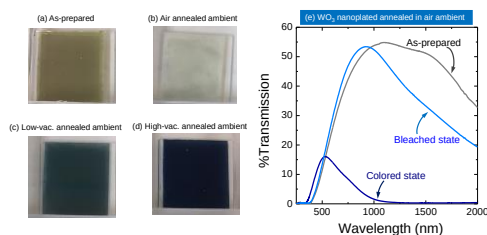


Figure 4. (a)-(d) Photographs of all prepared sample on ITO coated glasses substrate and (e) Transmittance spectra of as-prepared, colored and bleached for the system of annealed glass/ITO/ WO_3 nanoplate at air ambient

Conclusions

In conclusion, the single crystalline WO_3 nanoplates were fabricated by acid treatment and post annealed treatment at different ambient. The XRD revealed that monoclinic WO_3 nanoplates present after annealed treatment. Meanwhile FE-SEM and TEM results show that the all prepared samples was square shape. The WO_3 nanoplate annealed at low and high vacuum ambient have the blue color due to the stoichiometry. Furthermore, the WO_3 nanoplates annealed in air ambient exhibits the electrochromic property and therefore may be used in practical electrochromic smart window applications.

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