Journal of Metals, Materials and Minerals, Vol. 31, No. 2, pp. 123-128, 2021

Electrochromic property of tungsten trioxide films prepared by DC magnetron sputtering with oblique angle deposition and thermal oxidation

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Received date:
15 February 2021
Revised date
21 April 2021
Accepted date:
23 April 2021

Keywords:
Magnetron sputtering;
WO_3 film;
OAD;
Electrochromic;
Thermal oxidation

Abstract

In this work, WO_3 thin films were prepared in two steps: First, tungsten (W) films with thickness of 100-300 nm were deposited by DC magnetron sputtering with oblique angle deposition (OAD) technique at 0° and 85°. Second, sputtered W films were annealed under air atmosphere at a temperature of 500°C and different oxidation times for 1-3 h. The structure of WO_3 thin films were examined by X-ray diffraction and field emission scanning electron microscope. In addition, the optical and electrochromic properties of the WO_3 thin films were measured by a spectrophotometer before and after testing in potassium hydroxide electrolytes. The results showed that the OAD technique can enhance porosity and exert high oxidation in W films. The increase in film thickness and oxidation time indicated that the crystallinity of WO_3 films increased. The condition of WO_3 films for OAD at 85°, thickness of 300 nm, and oxidation time of 1 h showed the best electrochromic property with the highest optical modulation and current density.

1. Introduction

Nowadays, thin films play a big role in the industry, and applications and coating technology need to be developed to maximize their benefit. Among the developments is the creation of smart glasses, such as suspended-particle devices, liquid crystals, and electrochromic devices, which can alter its optical property by controlling electricity. However, smart glasses are photochromic [1] and thermochromic [2], i.e., sensitive to sunlight and heat, respectively, which are hard to control by human. Liquid crystals and suspensions require a continuous operating voltage, thus consuming energy throughout their use. By contrast, electrochromic devices can alter from being transparent to translucent and vice versa without requiring a continuous voltage at a fast response rate. Smart glasses consist of multilayer thin films, such as a layer of transparent electrodes, which can conduct electricity from a metal oxide, charge-collection layer/electrolyte film, and electrochromic layer that allows changing colors [3].

WO_3 films are widely used in the electrochromic layer because it provides good optical properties, high coloration efficiency, high ion capacity, and fast response time using low electricity [4]. In general, WO_3 films have good electrochromic properties, such as amorphous structure, fast response, and good optical modulation, and have easy degradation when tested in an electrolyte solution [5]. Conversely, the crystal structure of WO_3 films show a slow response and bad electrochromic property but high durability in an electrolyte solution [6,7].

Ou *et al.* [6] attempted to improve the nanostructures of WO_3 films, which were prepared through anodization of sputtered W films, external substrate heating, and annealing. The prepared WO_3 films had a high surface area and showed high electrochromic properties and good stability. However, the process is complex and require a lot of equipment. Salazar *et al.* [8] showed that porous WO_3 films can be obtained through the oblique angle deposition (OAD) technique. This technique enhances the surface area of WO_3 films, but the obtained films have a low deposition rate and exhibit amorphous structure.

In this respect, here, we report a simple process to achieve WO_3 films with more crystallinity and porous structure. W films were deposited on fluorine-doped tin oxide (FTO) glass substrate via DC magnetron sputtering technique combined with OAD. The W films were successfully prepared to WO_3 with a porous crystal structure after the thermal oxidation process. The effects of film thickness and oxidation times on the optical and electrochromic properties of WO_3 films were investigated.

2. Experimental details

2.1 Film deposition

The FTO coated glass was ultrasonically cleaned sequentially in acetone, isopropyl alcohol, and deionized water for approximately 15 min each. The W films were deposited using the W target (99.95%

DOI: 10.14456/jmmm.2021.29

purity, 2 inches diameter, and 0.25 inches thickness; Kurt J. Lesker, Company) on the FTO substrates via DC magnetron sputtering with the OAD technique. The OAD of dense film (referred as sample D) at 0° and the OAD of porous film (referred as sample P) at 85° were compared, as shown in Figure 1. The vacuum chamber was evacuated via coupled diffusion and rotary pumps until a base pressure of 5×10^{-5} mbar was achieved. An Ar (99.999% purity) gas was introduced in the chamber at a constant flow rate of 15 sccm while using a mass flow controller (Aalborg GFC17). Sputtering power was kept at 20 W through OAD at 0° and 85°. The W target was pre-sputtered for 3 min to remove oxide on the target surface. The thicknesses of the W films for both OAD conditions were 100 and 300 nm. The sputtered W films were thermally oxidized at a temperature of 500°C in ambient air with various oxidation times for 1, 2, and 3 h. The deposition conditions of the WO_3 films are listed in Table 1.

2.2 Film characterizations

The prepared films were confirmed to the crystal structure of WO_3 films via X-ray diffraction using Cu-Kα radiation at λ of 1.54184 Å (Bruker, D2 PHASER) determined at 2θ from 20° to 80°. The elemental composition of the oxygen/tungsten (O/W) ratio was measured by an energy-dispersive X-ray spectrometer. The physical morphology of the WO_3 films was obtained by a field emission scanning electron microscope (FE-SEM, TESCAN MIRA-3, Czech Republic). The optical transmittance spectra and electrochromic property of the WO_3 films were measured using an ultraviolet–visible spectrophotometer (GENESYS 10S, Thermo Scientific) in the spectral region between 200 and 1100 nm by applying voltages of −1.5 and +1.5 V. The potential was adjusted to −1.5 V for 20 s of the colored state and then switched to +1.5 V for 20 s of the bleached state in 0.1 M of potassium hydroxide (KOH) electrolyte solution. Finally, cyclic voltammetry (CV) measurements were performed under applied voltage from −1.5 V to +1.5 V at a scan rate of 100 mV/s using KOH as an electrolyte with the WO_3 films as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode.

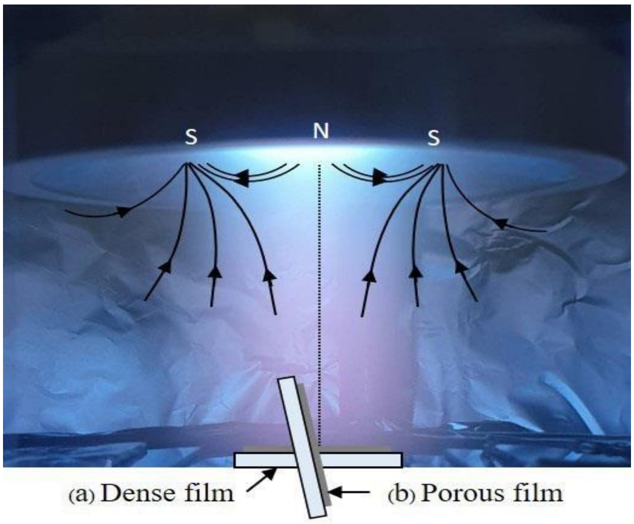

Figure 1. Schematic of the W films deposited by DC magnetron sputtering with OAD at (a) 0° (dense film) and (b) 85° (porous film).

3. Results and discussion

3.1 Physical morphology of the W films

The W films were deposited on an FTO glass substrate with a sputtering power of 20 W through OAD at 0° and 85°, which generated different deposition rates and physical morphology. The deposition rate decreased from 13.79 to 6.90 nm·min^{-1} when OAD was changed from 0° to 85°, which is attributed to the decreasing adatom flux onto the substrate. Moreover, the density of the W films decreased from the shadowing effect and limited adatom diffusion on film morphology [8,9]. Dense and porous W films from the top-view and cross-sectional FE-SEM images were revealed, as shown in Figure 2. It is attributed to the self-shadowing of adatom with an OAD at 85°, and the surface showed dominant roughness and small void, which indicated a high surface area.

Table 1. Deposition conditions of WO_3 films.

Samples	Sputtering power (Watt)	Ar flow (sccm)	Film thickness (nm)	OAD (°)	Thermal oxidation (°C)	Oxidation time (h)
D1-1	20	15	100	0	500	1
D3-3	20	15	300	0	500	3
P1-1	20	15	100	85	500	1
P3-1	20	15	300	85	500	1
P3-2	20	15	300	85	500	2
P3-3	20	15	300	85	500	3

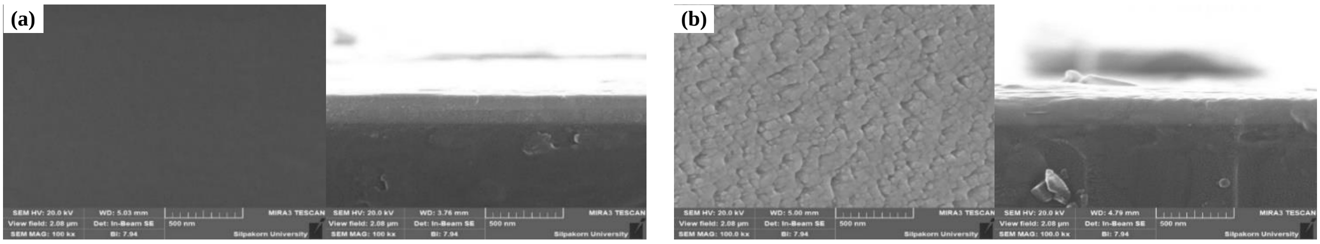

Figure 2. Top-view and cross-sectional FE-SEM images of (a) D1 and (b) P1.

Figure 3 clearly shows the influence of the OAD technique on the transparency of W films after the thermal oxidation process. The samples D1-1 and P1-1, and P3-3 exhibited change in the optical property, transforming from opaque W films to transparent WO_3 films, but the sample D3-3 retained its opaque films. These results indicate that the thermal oxidation is not sufficient to convert the W films according to their film thickness as used in the experiment (300 nm).

3.2 Elemental composition and crystal structure

Figure 4 shows the elemental composition of samples changing from D1 to D1-1 and P1 to P1-1. The oxygen content in the W films increased after the thermal oxidation and turned to that of WO_3 films with the rearrangement of the atom. Although these samples were transparent, P1-1 exhibited an O/W ratio of 0.347%, which is higher than that of D1-1, i.e., 0.322%. The slightly different O/W ratios are attributed to the relatively low thickness of 100 nm and the high oxidation temperature of 500°C for 1 h, which is sufficient for the thermal oxidation throughout the W layer. However, OAD at 85° was proven to promote porous films and allow more oxygen to diffuse into the W films.

The X-ray diffraction (XRD) patterns of P1-1, P3-1, P3-2, and P3-3 are shown in Figure 5. The XRD results indicate that all samples had nanocrystallinity of monoclinic WO_3 films (JCPDS card no. 85-0950) at 2θ of approximately 23.10°, 23.58°, and 24.35°, which correspond to given index values of (002), (020), and (200), respectively. The intensity of the hkl plane was improved with increased film thickness and oxidation time, whereas all samples showed a dominant plane of (002).

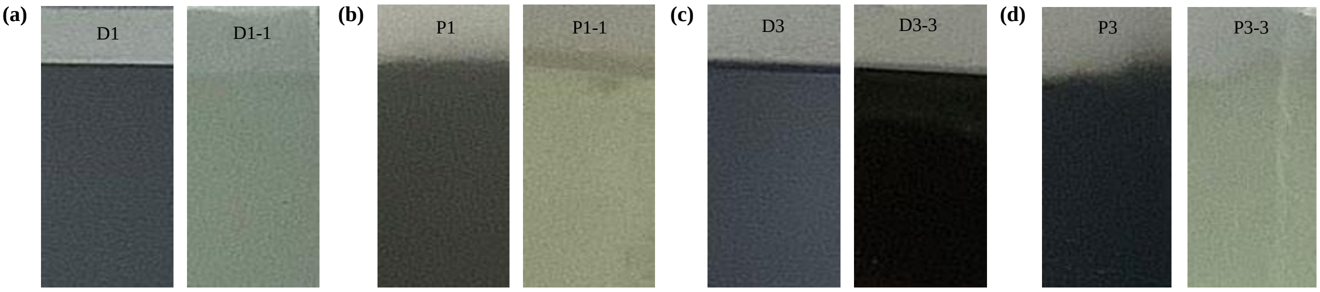

Figure 3. Photograph before (left) and after (right) the thermal oxidation of W films ((a) D1, D1-1, (b) P1, P1-1, (c) D3, D3-3, and (d) P3, P3-3).

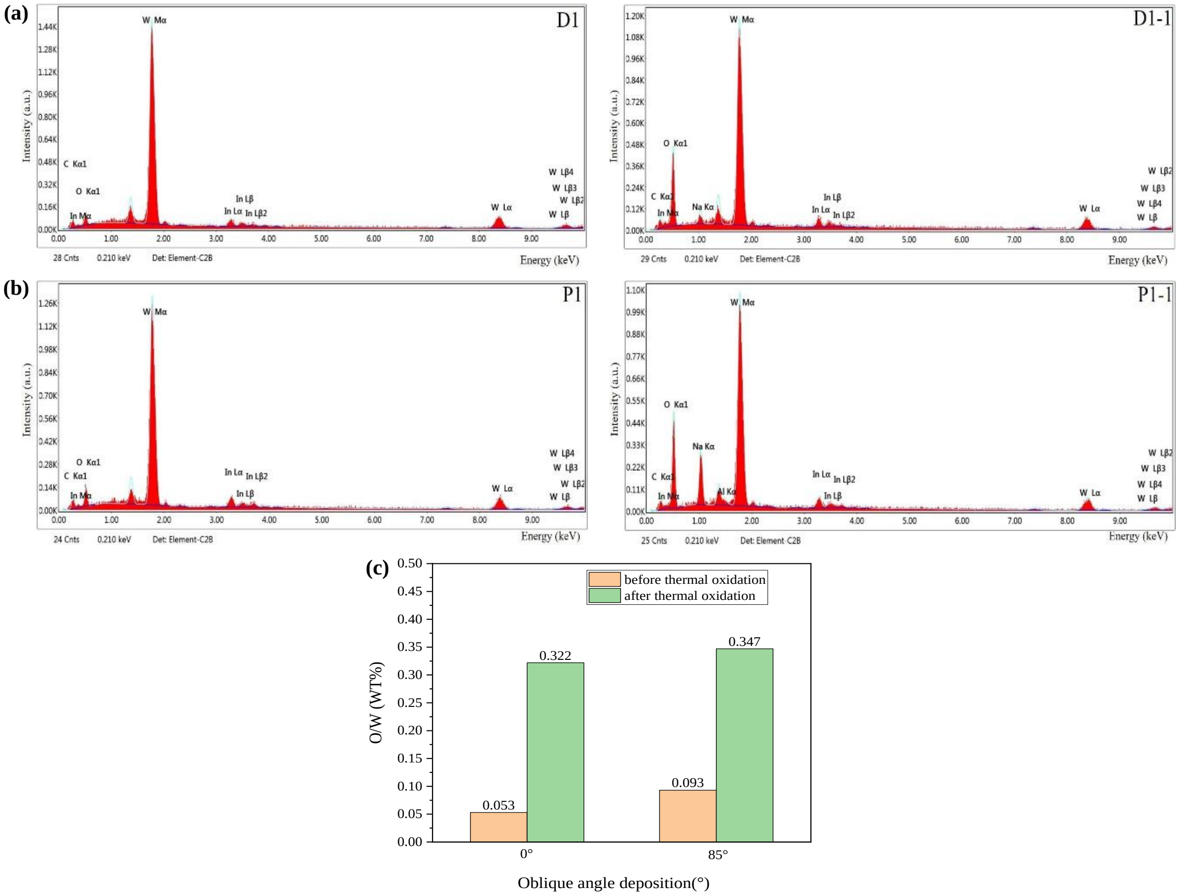

Figure 4. Energy-dispersive X-ray spectrum before and after thermal oxidation: (a) D1, D1-1; (b) P1, P1-1. (c) Atomic ratio of O/W.

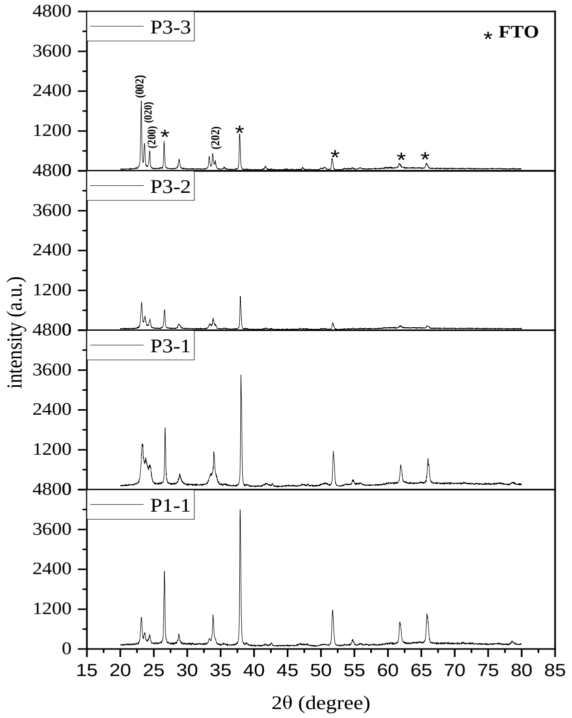

Figure 5. XRD patterns of P1-1, P3-1, P3-2, and P3-3.

3.3 Optical and electrochromic properties

The electrochromic property of the WO_3 films were measured by testing under colored/bleached states. The optical transmittance spectra of P1-1, P3-1, P3-2, and P3-3 in the wavelength range of 200-1,100 nm are shown in Figure 6. The electrochromism of WO_3 films can be switched reversible to a colored state (deep-blue) through the insertions of ions (K^+) and electrons (e^-) to form tungsten bronze (KWO_3) according to the reaction described by Equation (1). The reduction of the W^{6+} state to the W^{5+} state affected their optical absorption, which was caused by the small polaron transitions between the W^{6+} and W^{5+} states [10].

$$WO_3 + K^+ + e^- \leftrightarrow KWO_3 \qquad (1)$$

The results showed the high optical transmittance of the as-deposited films of P1-1 due to lowest film thickness. At a thickness of 300 nm, the optical transmittance spectra of WO_3 films were approximately the same, and the oxidation time was not significantly affected. To determine electrochromic property [6], the change in the optical density in the colored and bleached states were calculated by Equation (2):

$$\Delta OD = log\left(\frac{T_b}{T_c}\right) \qquad (2)$$

where T_b is the bleached state and T_c is the colored state at wavelengths of 750 and 1,050 nm.

A high value of ΔOD at 1,050 nm corresponding to near infrared was found at 0.51 of P3-1, and it decreased to 0.33 and 0.24 for P3-2 and P3-3, respectively. At a wavelength of 750 nm, ΔOD decreased in the order of samples P3-3 > P3-1 > P3-2 (0.22 > 0.16 > 0.13, respectively). These results were relatively similar and consistent with the XRD results with increasing crystallinity of films. The change in the colored and bleached states for P1-1, P3-1, P3-2, and P3-3 is shown in Figure 7.

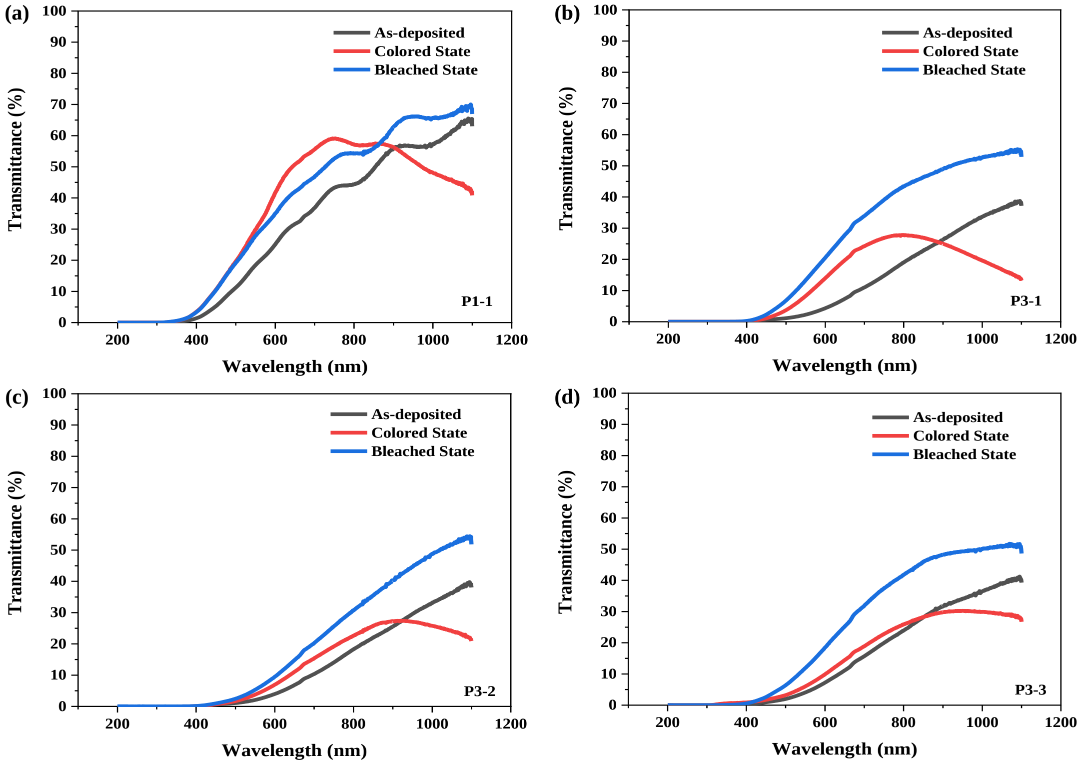

Figure 6. Transmittance spectra of the as-deposited, colored, and bleached states of WO_3 films at (a) P1-1, (b) P3-1, (c) P3-2, and (d) P3-3.

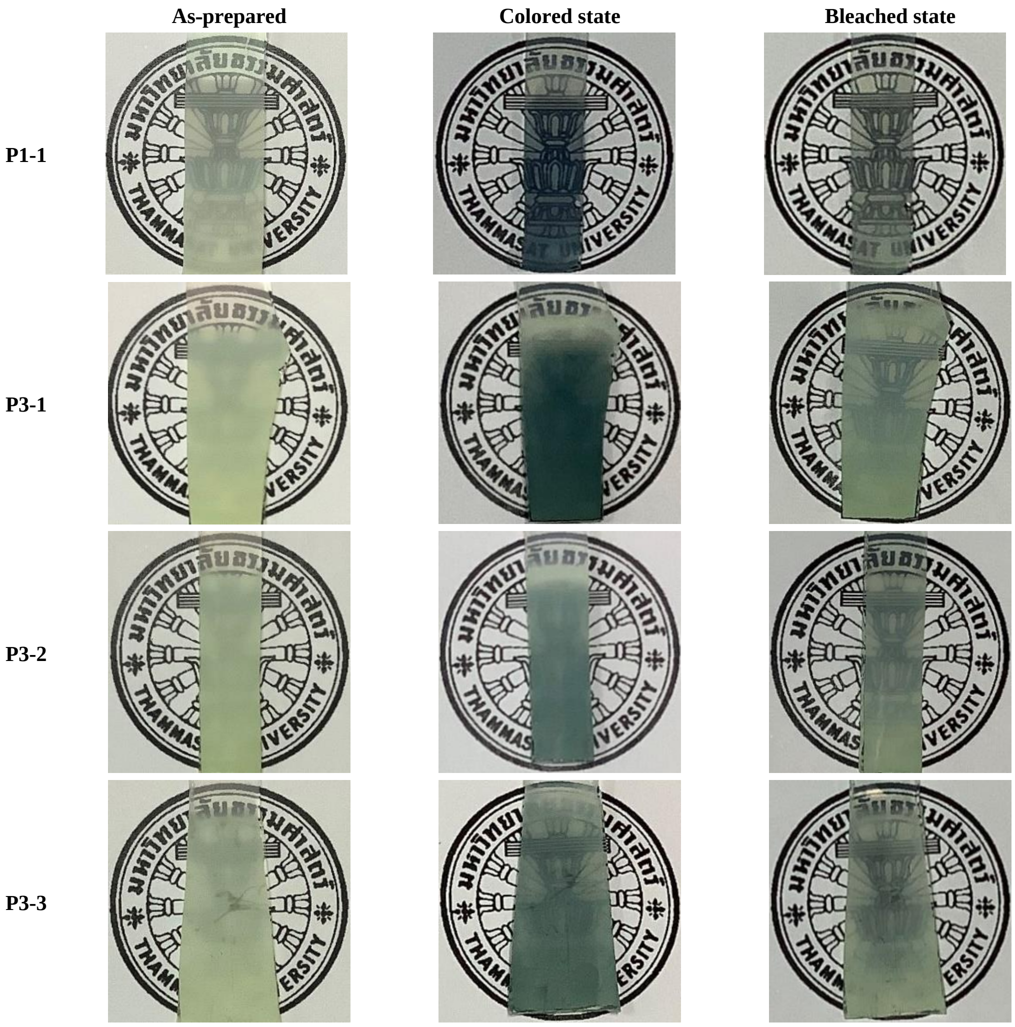

Figure 7. Photographs of the WO_3 films of the as-deposited, colored, and bleached states for P1-1, P3-1, P3-2, and P3-3..

Figure 8 shows the CV curves of P3-1, P3-2, and P3-3, where the cathodic current at the negative potential decreased when the oxidation time was increased. The largest amount of ion intercalation could be obtained from the largest cathodic current peak and area [11]. Therefore, P3-1 shows the best electrochromic property. The electrochromic properties decreased as the film had a high crystallinity due to the orderly structure, making it more difficult for ions to penetrate [7].

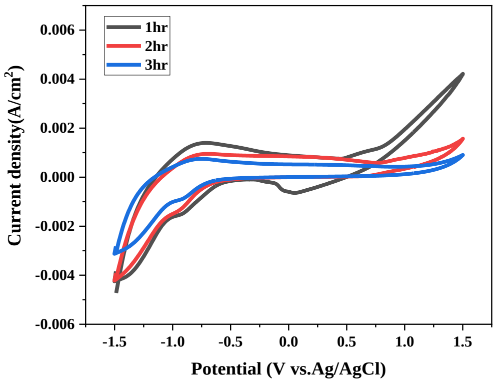

Figure 8. Cyclic voltammetry of WO_3 films in 0.1 M of KOH at a scan rate of 100 mV/s for P3-1, P3-2, and P3-3.

4. Conclusions

WO_3 films were successfully prepared from thermally oxidized W films via sputtering with OAD at 85°. The W films with a thickness of 100 nm underwent OAD at 0° and 85° and were transformed to WO_3 films after 1 h thermal oxidation at a temperature of 500°C. For 300 nm thick W films, only the OAD at 85° could be thermally oxidized to the transparency of WO_3 films. The OAD at 85° enhanced the oxidation of the W films, and the oxidation time improved the crystallinity of the WO_3 films. P3-1 exhibited good electrochromic properties with high optical modulation and high current density.

Acknowledgment

We gratefully acknowledge the funding from Thammasat University Research Fund (Contract No. TUFT 032/2563). The authors would like to thank the Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi and the Nation Electronics and Computer Technology Center (NECTEC) for providing the experimental facilities.

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