บทความวิจัย

A STUDY OF WO_X FILMS PREPARED BY SPRAY PYROLYSIS FOR ELECTROCHROMIC DEVICE

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ABSTRACT

In this work, tungsten oxide (WO_X) films were deposited on glass substrates by spray pyrolysis technique. Alkoxide ($WCl_6(OC_2H_5)$) solution was used as WO_X precursor and sprayed on 25.4 mm x 76.2 mm glass slide. The alkoxide concentrations and volumes were varied from 10 to 40 mM and 50 to 150 ml, respectively. The substrate temperatures were set at 150, 200 and 250 °C. The spray pressure was adjusted at 0.15 MPa and sprayed with an 8% duty cycle (1-second ON and 11-second OFF in a cycle) to keep substrate temperature unchanged. The crystal structure, optical properties, surface morphology and elemental analysis were then characterized by X-ray diffractometer (XRD), UV-visible spectrophotometer, scanning electron microscope (SEM)and energy dispersive spectrometer EDS), respectively.The X-ray diffraction results showed that the as – deposited films were amorphous structures. After annealing at the temperature of 500 °C for 2 hours, the WO_3 diffraction peaks at (200), (112), (202), (140) and (142) planes indicated the monoclinic crystal structure. The transmittance decreased due to increased film thickness as the solution volume increased. However, the transmittance increased at higher substrate temperature due to lower film thickness resulted from droplet evaporation. Furthermore, the energy band gaps (Eg) of the films were calculated to be between 3.70 – 3.81 eV. The results of elemental analysis found that the amount of tungsten and oxygen increased with increasing film thickness. The suitable solution concentration, substrate temperature and solution volume were 20 mM, 250 °C and 100 ml, respectively. This condition, was used for preparing WO_X film on ITO substrate and then testing coloration with the applied voltage of 1.0 Volt. It was

suggested that the tungsten oxide film could be used as an electrochromic device due to the color change with high contrast when the electric field was applied to the film.

Keywords: spray pyrolysis, tungsten oxide, electrochromic device

Introduction

Tungsten oxide thin film is one of a very popular material in the electrochromic devices application. The color of film is based on electrical properties, transmittance and the structure of the film. It was found that light transmission could be reduced with increased reflectivity. Therefore, it is preferable to apply tungsten oxide thin film for electrochromic: smart windows, office glass rearview mirror, various display screens and electronic paper (Nanotec, 2015).

Thin film tungsten oxide has been grown by various techniques including evaporation (Arfaoui et al., 2015), sputtering (Madhavi et al., 2014), electrodeposition (Fan Jiang et al., 2015), anodization (Nadja et al., 2015), sol-gel deposition (Kai Huang et al., 2007), chemical vapor deposition (CVD)(Stoycheva et al.,2014), and spray pyrolysis (Regragui et al., 2003). In this work, the tungsten oxide thin films were prepared by spray pyrolysis method. The effect of solution volume and substrate temperature were studied. After prepared films with the different conditions, the films were then characterized the crystal structure, optical properties, surface morphology and elemental analysis by using X-ray diffractometer (XRD), uv-visible spectrophotometer, scanning electron microscope (SEM) and energy dispersive spectrometer (EDS), respectively. This optimized condition was used to prepare WO_X films on ITO substrates and then testing coloration with the applied voltage of 1.0 Volt.

Methods

Tungsten oxide thin films preparation was carried out in to two steps. The first step was preparing alkoxide ($WCl_6(OC_2H_5)$) solution by diluting tungsten chloride powder (WCl_6 ; $\geq$ 99.9%, Aldrich) in ethanol (C_2H_5OH ; absolute for analysis, Emsure®) 250 ml at 60 – 70 °C by heating and stirring for 24 hour until the solution became clear. The tungsten chloride concentration was optimized to be 20 mM throughout this work.

The second step was the films deposited on glass slide by spray pyrolysis technique. Start with cleaning of 25.4 x 76.2 mm glass slide by degreasing with pH neutral detergent and then ultrasonically cleaning in deionized water and acetone (C_3H_6O ; for analysis, Emsure®), followed by drying with the electric hair dryer. The sprayed pressure was adjusted at 0.15 MPa and sprayed with an 8% duty cycle (1-second ON and 11-second OFF in a cycle) to keep substrate temperature unchanged. The deposition parameters were presented in Table 1.

Table 1 The deposition parameters.

Sample	Substrate temperature (°C)	Solution volume (ml)
W_{G1}	150	100
W_{G2}	200	100
W_{G3}	250	100
W_{G4}	250	50
W_{G5}	250	150
W_{ITO1}	150	100
W_{ITO2}	200	100

The optical transmittance was characterized using a HALO VIS-20 visible spectrophotometer with the scanning wavelength range between 320 – 1100 nm. The surface morphology, thickness and elemental analysis of these films were analyzed using a JSM-6610LV JEOL scanning electron microscope. The crystal structures were characterized with X-ray diffractometer (Rigaku- Miniflex)

For the coloration investigation, the films were deposited on ITO-glass substrate with a sheet resistance of 7 Ω/□ and the transmittance was about 84%. The samples were set in the planar configuration using copper plate as an electrode. The 0.1 M of KCl solution was used as electrolyte and applied the potential of 1.0 Volt between the sample and copper plate.

Results and Discussion

Optical Transmittance of WO_x films

Figure1 shows the transmittance of WO_x films prepared when substrate temperatures were varied as 150, 200 and 250 °C at the same solution volume of 100 ml. The transmittance increased at higher substrate temperature due to lower film thickness resulted from droplet evaporation. This results were also confirmed with the cross - section image in Table 3 and Figure 5.

Figure 2 shows the transmittance of WO_x films prepared with different solution volumes. The solution volumes were varied as 50, 100 and 150 ml at the fixed substrate temperature of 250 °C. The transmittance decreased due to the increased of film thickness as solution volume increased. This results were confirmed by the SEM cross - section image in table 4 and Figure 6.

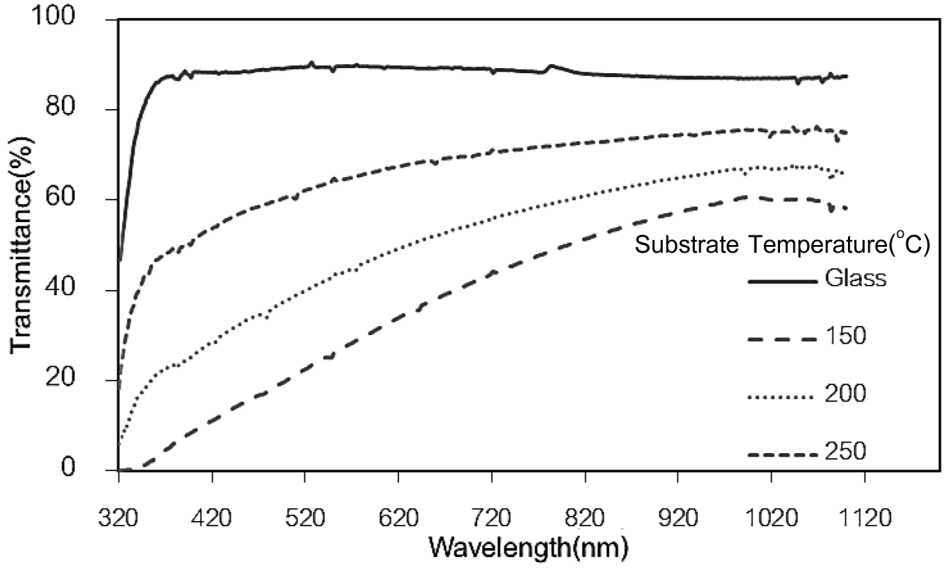


Figure 1 The optical transmittance of WO_x films prepared with different substrate temperature at the same solution volume of 100 ml.

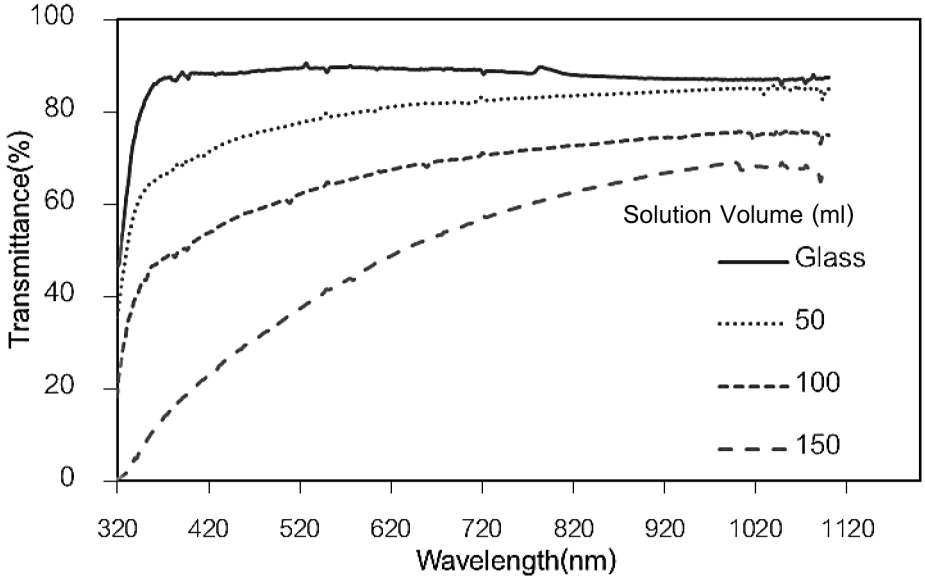


Figure 2 The optical transmittance of WO_X films prepared with different solution volume at the same substrate temperature of 250 °C.

Table 2 represents the energy band gaps (Eg) of WO_X films deposited on glass slide. The energy band gaps were between 3.70 – 3.81 eV.

Table 2 The energy band gap (Eg) of tungsten oxide thin films prepared on glass substrate.

Sample	Substrate temperature (°C)	Solution volume (ml)	The energy band gap (eV)
W_1	150	100	3.75
W_2	200	100	3.73
W_3	250	100	3.81
W_4	250	50	3.74
W_5	250	150	3.70

The energy band gap “Eg” has been calculated from the transmission spectra by using equation below:

$$(\alpha h\nu)^{1/m} = A(h\nu - E_g) \qquad (1)$$

According to Eq, (1), where A is constant value, **hv** is the photon energy, α is the absorption coefficient of the WO_X film and “m” depends on transition nature. For the presently studied films fit of $(\alpha h\nu)^{1/m}$ vs **hv** was obtained with m = ½ for direct energy band gap. The extrapolation of the linear part of the curve to zero absorption coefficient and gives Eg. The average value of Eg were 3.75, 3.73 and 3.81 eV, when the substrate temperature increased and were 3.74 , 3.81 and 3.70 eV, when the solution volume increased as shown in figure 3

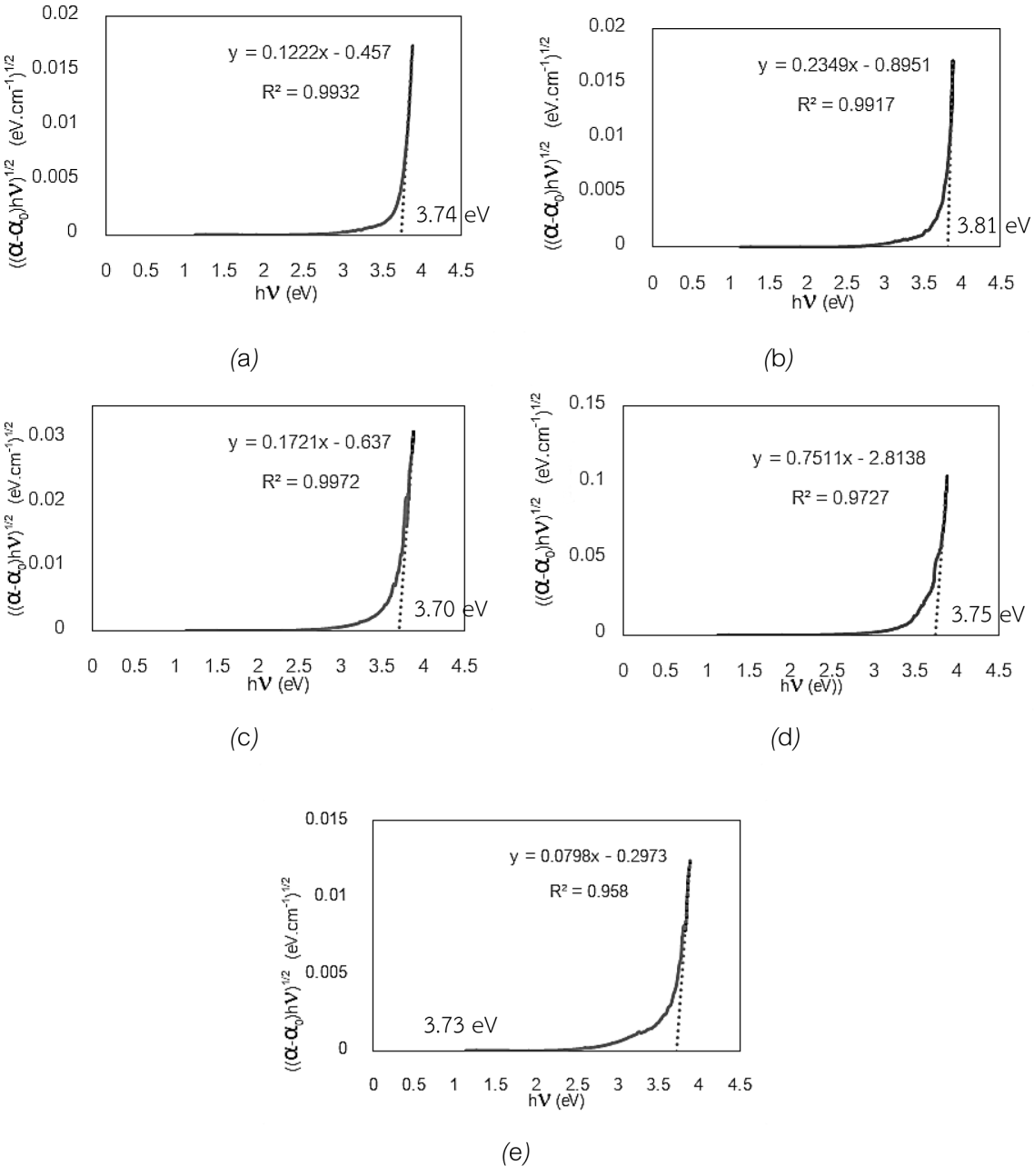


Figure 3 The energy ban gaps of WO_X films. (a) (b) and (c), The samples were prepared at the substrate temperature of 250 °C with varied solution volume of 50, 100 and 150 ml, respectively (d) and (e), The samples were prepared at the same solution of 100 ml with substrate temperatures of 150 and 200 °C, respectively.

Structural and morphological characterization of WO_x films

1. The structural characterization of WO_x films

The as-deposited films were dark-brown and amorphous structure. This results were confirmed by X-ray diffraction technique (XRD). After annealing under atmospheric pressure at 500 °C for 2 hours, the films became more crystallinity and represented the diffraction peaks along (200), (112), (202), (140) and (142) plane of WO_3 as shown in Figure 4

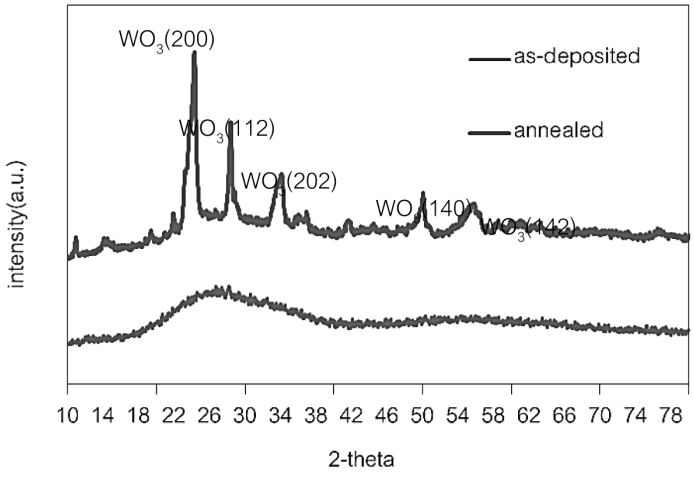


Figure 4 The X-ray diffraction pattern of as – deposited and annealed WO_x films.

2. Surface morphology of WO_x films

Table 3 showed surface morphology of WO_x films prepared at the different substrate temperatures. It was found that the grain size increased when the substrate temperature increased from 150 to 250 °C. Moreover, the grain size increased due to the film thickness increased when the solution volume increased as shown in Table 4.

Table 3 The surface morphology of WO_x films prepared with different substrate temperatures.

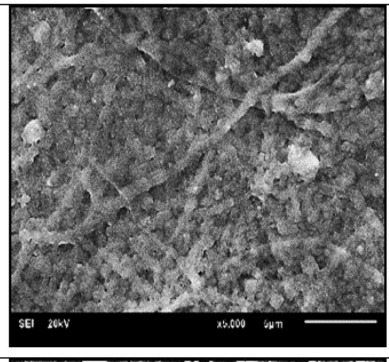
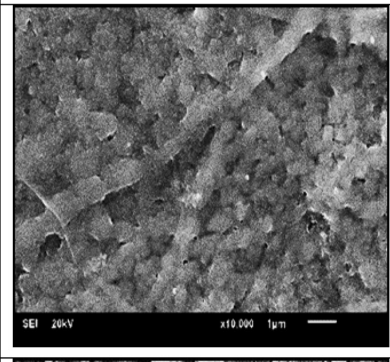
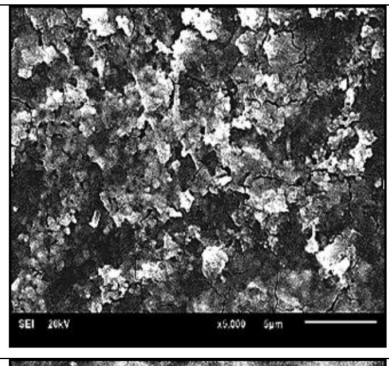
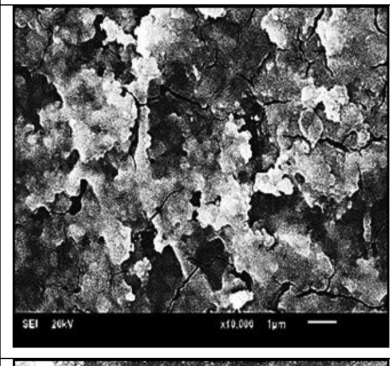
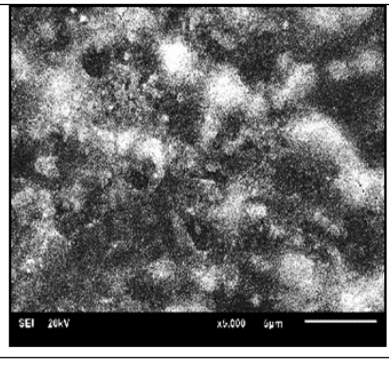
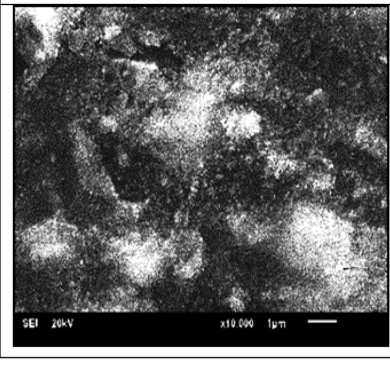
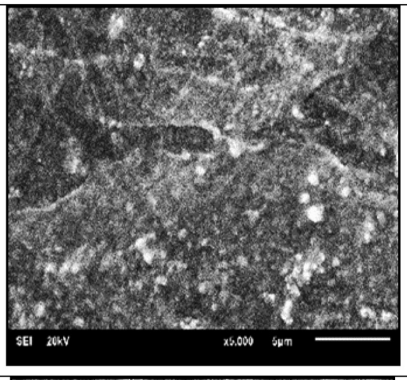
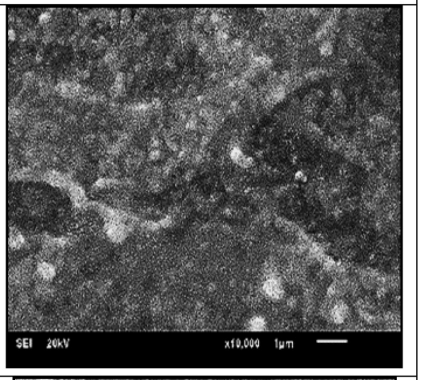
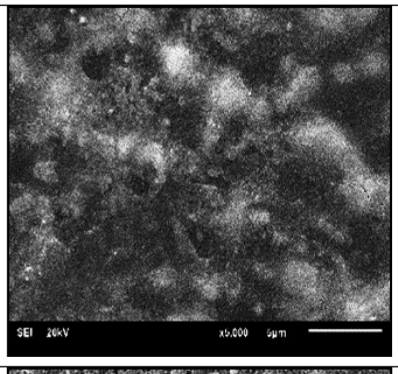
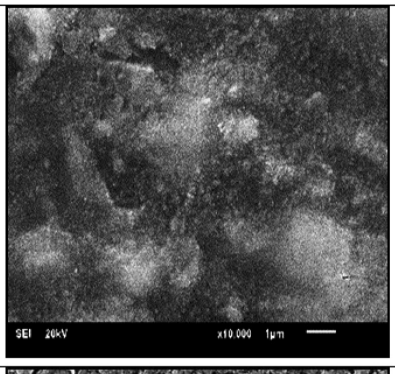
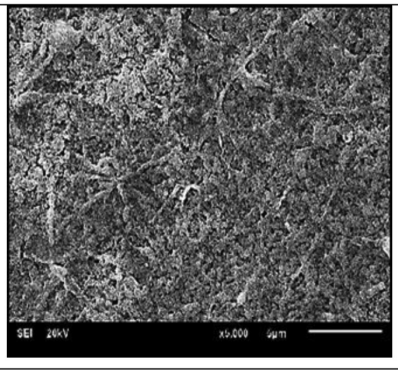
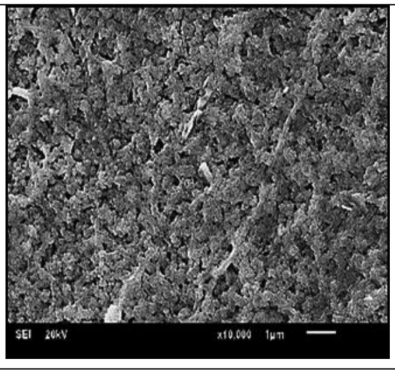
Substrate temperatures (°C)	Magnitude	
	X5,000	X10,000
150		
200		
250		

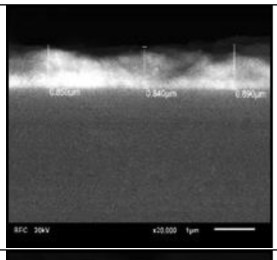
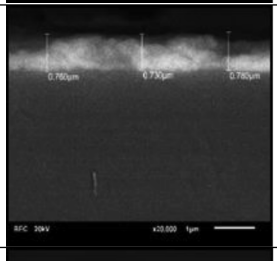
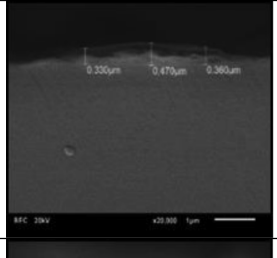
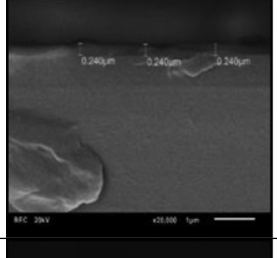
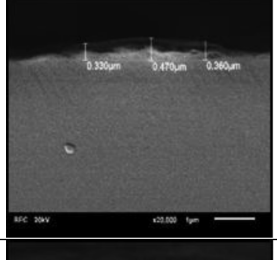
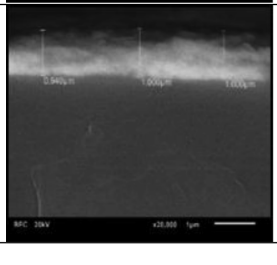
Table 4 The surface morphology of WOX films prepared with different solution volumes.

Solution volume (ml)	Magnitude	
	5,000X	10,000X
50		
100		
150		

3. Thickness and cross – section of WO_X films

The thicknesses and cross-section of WO_X films were shown in Table 5 and Figure 5 and 6.

Table 5 The average thickness of WO_X films prepared with different substrate temperatures and solution volumes.

Deposition conditions		Average thickness (nm)	X20,000
Substrate Temperatures	150	860 ± 26.456	
	200	757 ± 25.166	
	250	387 ± 73.711	
Solution volumes	50	240 ± 00.000 nm	
	100	387 ± 73.711 nm	
	150	980 ± 34.641 nm	

The results showed that the film thickness decreased when the substrate temperature increased as shown in Figure 5. It might be resulted from the higher evaporation rate of solution droplets when the substrate temperature increased could make some solution droplet dried and became a small solid particles blown out of coating chamber before incident on the substrate. In addition, the films thickness increased due to the solution volume increased as shown in Figure 6

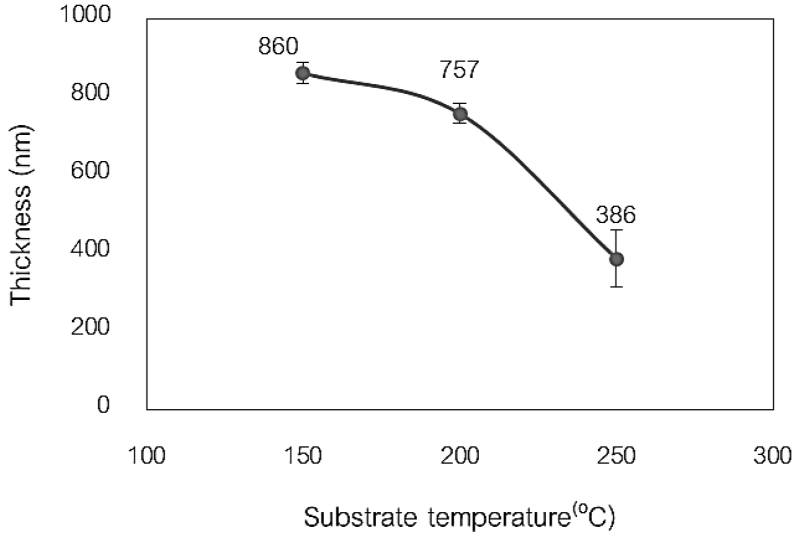


Figure 5. The thickness of WO_x films prepared with different substrate temperatures.

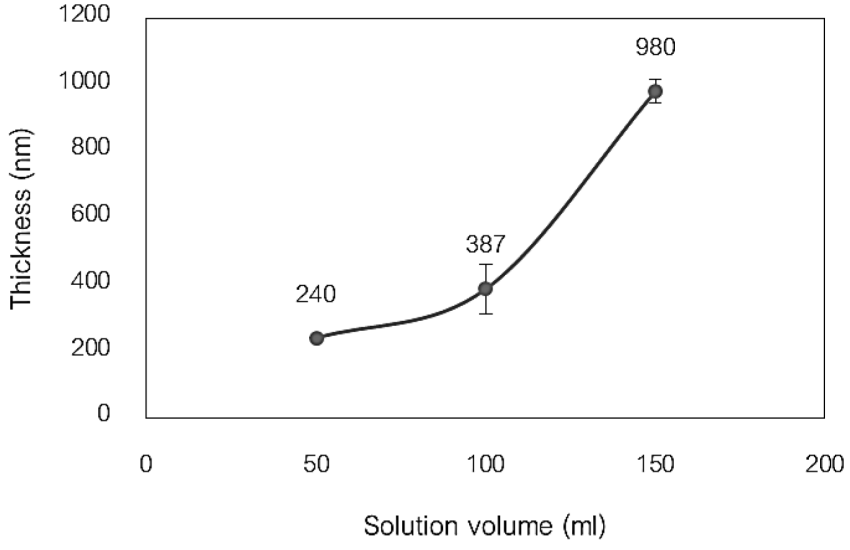


Figure 6. The thickness of WO_x films prepared with different solution volumes.

Elemental analysis

The amount of tungsten and oxygen decreased when the films thickness decreased due to the substrate temperature increased and the solution volume decreased as shown in Figure 7 and Figure 8

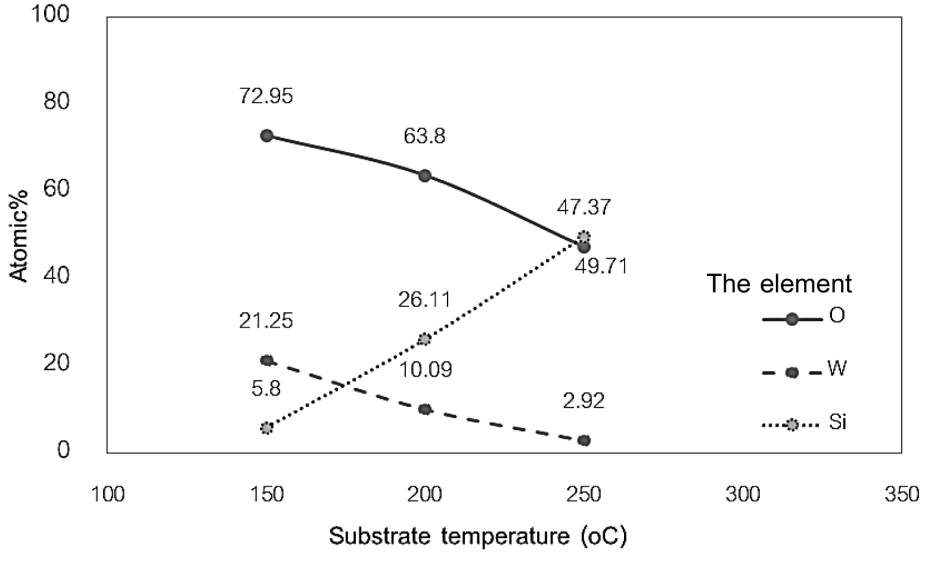


Figure 7 The atomic percent of tungsten, oxygen and tungsten and silicon when prepared WO_X film at different substrate temperatures.

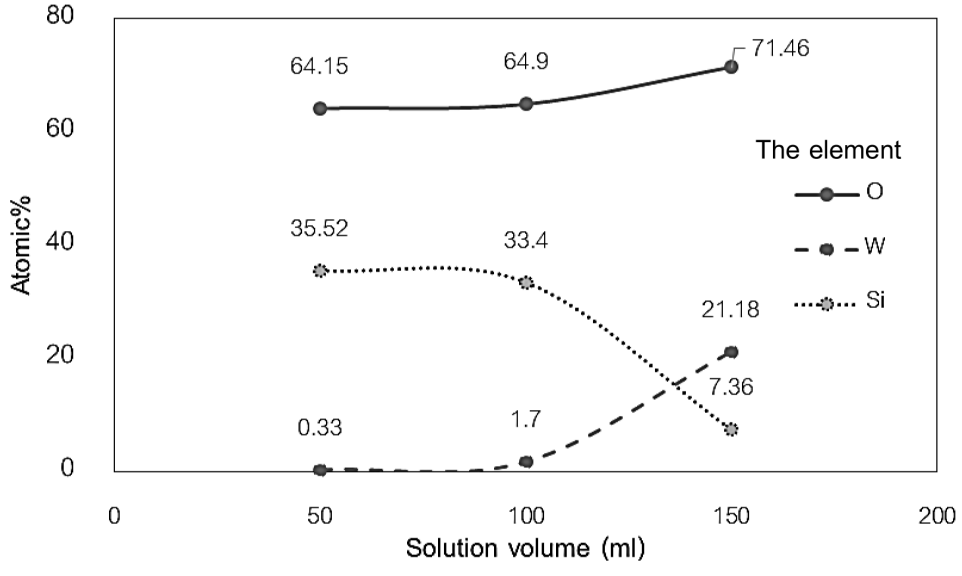


Figure 8 The atomic percent of tungsten, oxygen and tungsten and silicon when prepared WO_X films at different solution volumes.

Coloration Testing

The electrochromic chemical reaction can be expressed by the following equation:

$$WO_3 \text{ (transparent)} + xM^+ + xe^- \rightleftharpoons M_XWO_3 \text{ (blue)} \quad (2)$$

According to Eq.(2), where X is amount of charged ions per tungsten , M^+ is cation such as H^+, Li^+ or Na^+, WO_3 is tungsten oxide in a state of transparency or colorless, and M_XWO_3 is tungsten oxide in the state of coloration. (Tungsten oxide is formed as blue, which is called tungsten bronze).

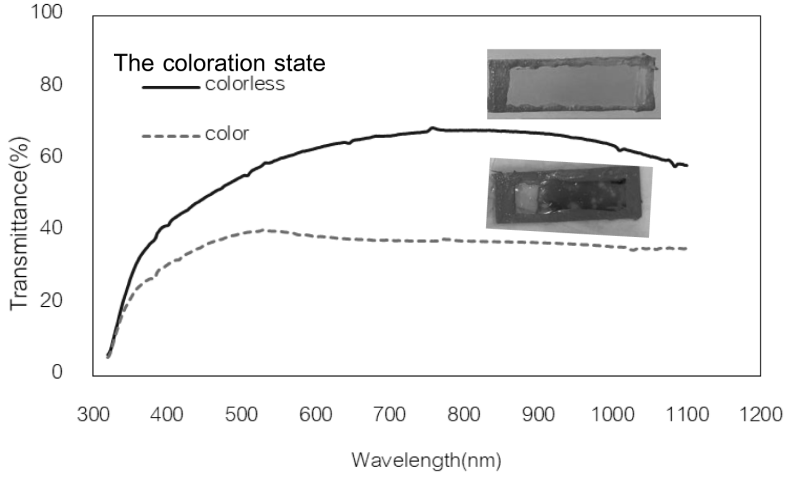


Figure 9 The coloration testing of WO_X films deposited on ITO substrate with the solution volume of 100 ml and substrate temperature of 150 °C.

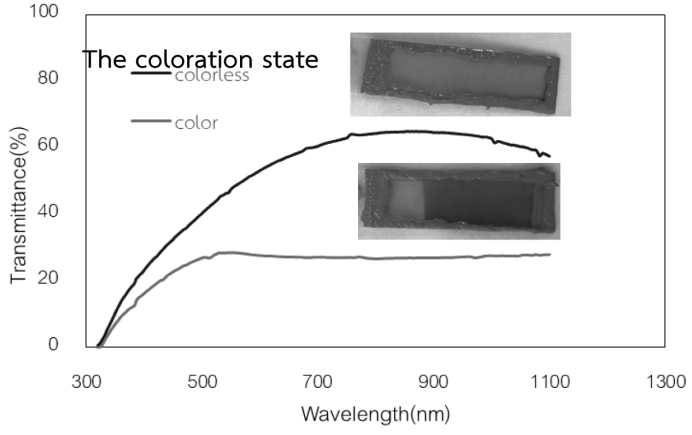


Figure 10 The coloration testing of WO_X films deposited on ITO substrate with the solution volume of 100 ml and substrate temperature of 200 °C.

Figure 9 and 10 showed the optical transmittance of coloration and de-coloration state of WO_X films when prepared at the substrate temperature of 150 and 200 °C using the same solution volume of 100 ml. It was found that, the tungsten oxide films prepared by spray pyrolysis could be used as the electrochromic device and the film prepared with the substrate temperature of 200 °C demonstrated the better electrochromism characteristic than 150 °C because of getting high contrast when changing the coloration state.

Conclusion

Tungsten oxide films can be successfully prepared by spray pyrolysis in this work. The energy ban gaps of tungsten oxide were calculated from optical transmittance in the range between 3.49 to 3.77 eV. The as – deposited films were amorphous structure and showed the diffraction peaks of WO_3 when anneal at 500 °C for 2 hours. The films thickness increased when the solution volume increased and the substrate temperature decreased. Tungsten oxide films can be used as the electrochromic device and change the color when applied the electric field to the films. It was found that the optimized the substrate temperature and solution volume in this work were 200 °C and 100 ml, respectively.

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