Electrochromic Properties of WO₃ Thin Film with Various Heat-Treatment Temperature†

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Tungsten oxide is a representative electrochromic material which has widely researched as an active electrochromic electrode. The electrochromic properties are related with ion intercalation and deintercaltion like lithium or proton ions. So, it is thought that amorphous or crystalline phase of tungsten oxide is very important for the capability and reversiblility of ion intercalation or deintercalaton. In this study, we analyzed the relationships between heat-treatment temperature and electrochromic properties of tungsten oxide film prepared by sol-gel coating method. It is concluded that amorphous phase shows superior intercalation or deintercalation capability to crystalline phase.

Key Words: Tungsten oxide, Electrochromic, Intercalation, Sol-gel, Electrochemical, Optical.

INTRODUCTION

Tungsten oxide (WO₃) is a representative electrochromic material which has widely researched as an active electrochromic electrode (working electrode). Ions like H^+ or Li^+ in electrolyte are intercalated into WO₃ thin film to reduce WO₃ to M_xWO_3, blue coloured state, when negative electric field is applied. Under positive electrical field, *i.e.*, the oxidated state, the reduced M_xWO_3 is oxidized and return to WO₃ original form[1-9].

$$xM^+ + xe^- + WO_3 \text{ (bleached)} \leftrightarrow M_xWO_3 \text{(coloured)}$$

Electrochromic behaviour of WO₃ was firstly discovered by Deb[1] in 1969 and has been researched extensively. WO₃ thin film could be coated by radio frequency sputtering, chemical vapour deposition and sol-gel coating method. In this research, we adopted sol-gel coating method, which is cost-effective and easy to control the composition of thin film. In the sol-gel coating method, tungsten metal is dissolved in hydrogen peroxide to obtain peroxotungstic acid and WO₃ thin film is coated onto indium tin oxide coated glass. There are dip coating, spin coating, spray coating and bar coating method in sol-gel coating method[10-17].

In this research, we coated WO₃ thin film by dip coating method and investigated the density and crystalline phase development by changing heat treatment temperature. The colouration efficiency of WO₃ thin film is known to be affected by charge density, which means that WO₃ thin film with low density and high porosity has a large charge density and shows a large transmittance change. An amorphous phase has larger

charge density than a crystalline phase, because ion carriers move in amorphous phase faster and more easily than in crystalline phase[10-20].

The main research aim is to study the effects of heat-treatment temperature to electrochemical and optical properties of WO₃ thin film. The density and porosity variations of WO₃ thin film was analyzed and transmittance change and electrochemical properties are also investigated when the heat-treatment temperature is changed.

EXPERIMENTAL

WO₃ sol and thin film coating: WO₃ precursor sol was synthesized by dissolving tungsten metal powder (99.9 %, Aldrich chemical company) in hydrogen peroxide (30 %, Junsei) and evaporating excessive hydrogen peroxide and water on hot plate at 150 ºC. The final product was a transparent orange coloured peroxotungstic acid solution. At the evaporation step, the temperature of solution should be controlled to maintain at 60-80 ºC, or yellow precipitates or white precipitates are generated which is considered as tungstic acid. The transparent orange peroxotungstic acid solution was added to ethanol and stirred for 1 h at room temperature, of which concentration was 1 M. Indium tin oxide glass (samsung corning, 12 Ω/γ, 180 nm) was dipped and withdrawed at 100 mm/min speed and was dried at 100 ºC for 10 min and heat-treated at 100-500 ºC for 1 h.

X-ray diffractometer (XRD KFX-987228-SE Mac science was used to investigate the crystallization behaviour of WO₃

thin film. The thickness was measured by observing cut-veiw image of WO₃ thin film by field emission scanning electron miscroscopy (FE-SEM) electochemical properties were measured by half-cell test method using Potentiostat/Galvanostat (PGASTAT 12, Autolab). The reference electrode was Ag/AgCl and counter electrode was Pt wire. Cyclic voltammetry (CV) analysis was conducted at voltage range of -1 V and +1 V and at a scan rate of 50 mV/s. Chronocoulometry (CQ) analysis was done at ±1 V for 30 s of holding time. *In-situ* optical properties were measured by irradiating He-Ne laser light with 633 nm wavelength and detecting the transmitted light power using optical power meter (Newport 1830-C). *Ex-situ* optical properties were analyzed by UV/VIS/NIR photospectrometr (V570, JASCO) at 200-2500 nm range of wavelength.

RESULTS AND DISCUSSION

Crystallization behaviour: The crystallization behaviour of WO₃ thin film coated on indium tin oxide glass was shown in Fig. 1. Until 300 ºC, WO₃ thin film was identified as an amorphous phase. At 400 ºC, it could be known to be crystallized as rhombohedral phase and the crystallinity became higher at 500 ºC and the crystalline phase did not change. As seen in the DTA and TG thermal analysis[14-17], XRD data showed that there exists as amorphous below 400 ºC and crystallized at 400 ºC. However, we could not find any evidence of monoclinic to rhombohedral phase transition at 400-500 ºC.
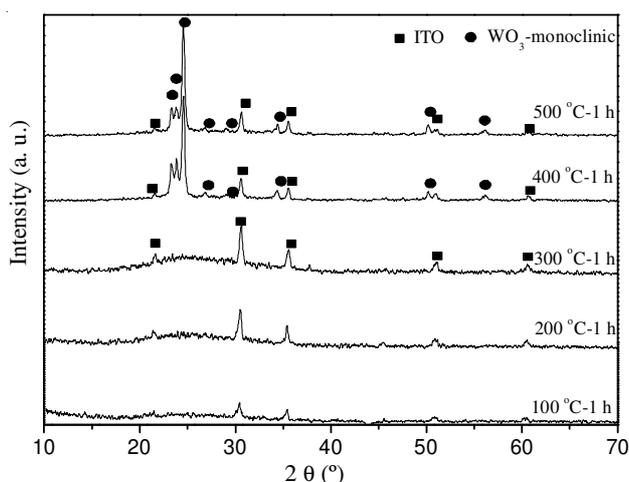

Fig. 1.　XRD pattern of as-prepared WO₃ thin film heat-treated at various temperatures

Film thickness and density variations with heat-treatment temperature: Fig. 2 shows the film thickness change of WO₃ thin film coated at 100 mm/min of withdrawal speed and heat-treated at 100-500 ºC was also studied. The film thickness was 285 nm at 100 ºC, tended to decrease to 255 nm at 200 ºC, 235 nm at 300 ºC, 210 nm at 400 ºC and there is no decrease at 500 ºC, 212 nm. It is considered that the increase in heat-treatment temperature removes more organic residues like CHx and densifies the thin film, so that the film thickness decrease with increasing heat-treatment temperature. At 400 ºC, a crystallization of the film occurred and the densification of the film almost finished that there is no decrease of film thickness at 500 ºC, which is consistent with differential thermal analysis data that is not presented in this paper[14-17].
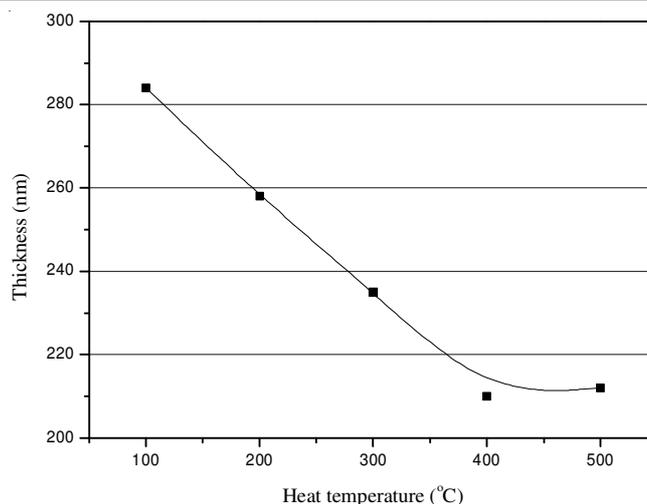

Fig. 2.　Thickness variations of WO₃ thin film with varying heat treatment temperature

The variations of density and porosity with heat-treatment temperature are shown in Fig. 3. The density at 100 ºC was 5.23 g/cm³, 5.42 g/cm³ at 200 ºC and 5.57 g/cm³ at 300 ºC and it increased abruptly to 6.79 g/cm³ at 400 ºC and decreased a little to 6.47 g/cm³ at 500 ºC. The trend of increasing density with heat-treatment temperature is similar to that of thickness decrease, as is shown in Fig. 2. The great increase of density at 400 ºC is considered to be related with the crystallization of amorphous phase to monoclinic phase. The porosity was 27 % at 100 ºC and decreased gradually to 22 % at 300 ºC and abruptly reduced to 5 % at 400 ºC and 9.7 % at 500 ºC.
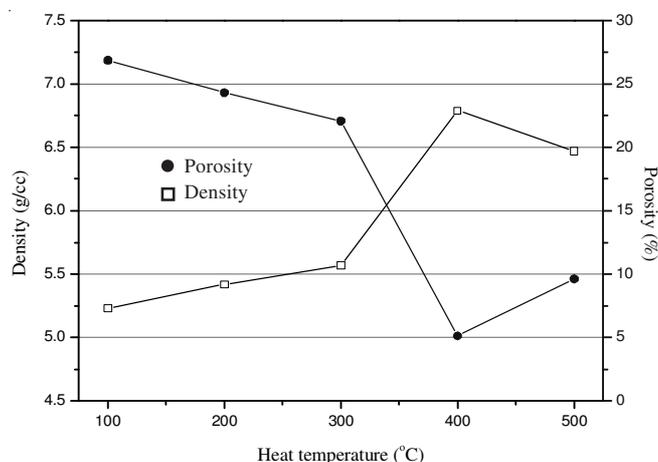

Fig. 3. Density and porosity of WO₃ thin film by heat treatment temperature

Electrochemical properties: Fig. 4 shows CV graphs of WO₃ thin film heat-treated at various temperatures, of which scan rate 50 mV/s. The oxidation current was 0.45 mA/cm² at -0.227 V for WO₃ thin film heat-treated at 100 ºC, 0.63 mA/cm² at -0.157 for 200 ºC, 0.56 mA/cm² at -0.08 V at 300 ºC. The reduction current increased from -0.57 mA/cm² at -1 V for 100 ºC to -0.77 mA/cm² at -1 V and remained to -0.75 mA/cm² at -1 V for 300 ºC. The maximum oxidation current and reduction current flowed for the film heat-treated at 200 ºC, which is considered to result from the removal of organic residuals in the film. It is thought that the heat treatment at 300 ºC made the film denser so that there is no increase of

current. The heat treatment at more than 400 ℃ reduced the oxidation and reduction current and showed small area of CV curves. It is thought to be due to the crystallization of WO₃ and the phase transition of monoclinic to orthorhombic phase.
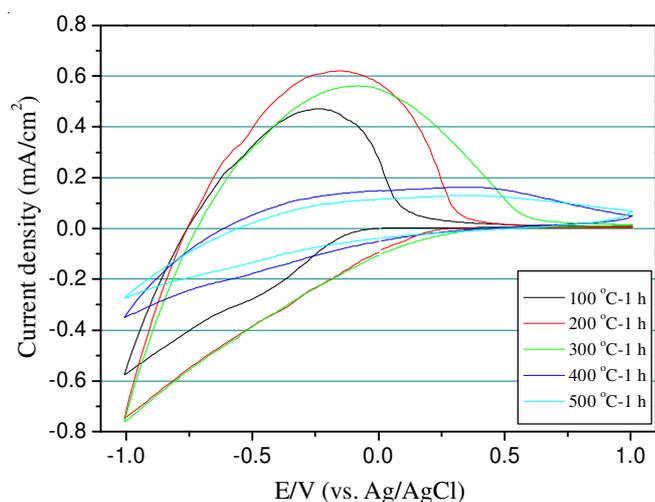

Fig. 4. Cyclic voltammetry of WO₃ thin film heat-treated at various temperature

Fig. 5 shows the charge density (CQ) variations of WO₃ thin film with heat-treatment when ± 1 V was applied for 30 s and *in-situ* corresponding light transmission at 633 nm He-Ne laser light. CQ tended to increase from 12.4 mC/cm² at 100 ℃ to 20.1 mC/cm² at 300 ℃, but decreased greatly to 8.64 mC/cm² and 7.67 mC/cm². It is thought that the increase in heat treatment temperature until 300 ℃ removes organic residues and causes a great increase in CQ, but the heat treatment above 300 ℃ is related with the crystallization of WO₃ which hinders the intercalation and deintercalation of lithium ions.

WO₃ thin film heat-treated at 100 ℃ showed 96 % of transmittance at bleached state and 15 % at coloured state and the film at 200 ℃ had 95 % at bleached state and 10 % at coloured state and the film at 300 ℃ showed the decreased transmittance, 80 % at bleached state and 8 % at coloured state. The crystallized film at 400 ℃ showed the bleached transmittance, 70 % and the coloured transmittance 24 %. The film at 500 ℃ showed 60 % of bleached transmittance and 21 % of coloured transmittance. In an amorphous phase of WO₃ thinfilm, the increase in heat treatment temperature decreased the transmittance of both bleached and coloured states. The increase of lithium ion intercalation decreased the transmittance at coloured state. The crystallization at more than 400 ℃ decreased the transmission difference between bleached state and coloured state. The heat-treatment more than 400 ℃ increased the density of film and accompanied the crystallization of amorphous phase. At 400 ℃, WO₃ film was crystallized from amorphous to monoclinic phase and the density increased largely and the porosity decreased. Therefore, lithium ion intercalation and deintercalation is difficult to occur in the crystallized film. At 500 ℃, the crystal phase transition occurs from monoclinic to orthorhombic, so that the transmission at coloured state decreased a little compared to that of 400 ℃.
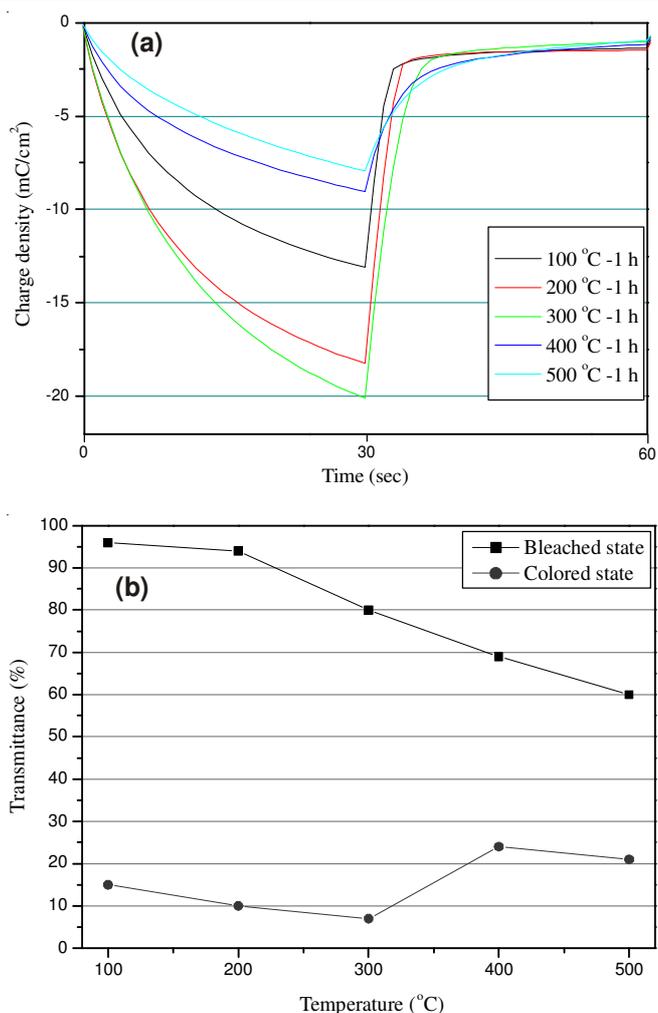

Fig. 5. Charge density (a) and transmittance variation (b) of WO₃ thin films heat-treated at various temperature

UV/VIS/NIR optical properties: Transmission variations with heat treatment temperature for WO₃ thin film that is as-prepared (a), coloured (b) and bleached (c) were shown in Fig. 6. For as-prepared WO₃ thin film heat-treated at 100-300 ℃, transmission spectra were almost similar, but the transmission decrease in the range of visible light was the greatest for the film heat-treated at 300 ℃, followed by 200 ℃ and 100 ℃. After bleaching, the film heat treated at 100 ℃ recovered their original state, although the transmission recovery at 800-1000 nm wavelength is not enough. WO₃ thin films heat-treated at 400 and 500 ℃ showed quite different light transmission behaviours. As-prepared WO₃ thin film heat-treated at 400 ℃ showed lower light transmission in the range of NIR and higher transmission at coloured state and lower transmission at bleached state, compared to that of WO₃ thin film heat-treated at 500 ℃. It indicates that lithium ion intercalation and deintercalation easily occur at WO₃ thin film heat-treated at 400 ℃ rather than that at 500 ℃. It means that orthorhombic phase has more accessible active sites for lithium ion than monoclinic phase. Transmission variations of as-prepared, coloured and bleached WO₃ thin film with heat-treatment temperature were summarized in Tables 1-3. Transmission difference between coloured and bleached was 32 % for 100 ℃ and 39 % for 200 ℃, 35 % for 300 ℃ and decreased abruptly

to 0.3 % for 400 ºC and slightly increased 3 % for 500 ºC. Ultraviolet ray shield was greater, the heat-treatment temperature higher. On the contrary, IR shield effects were higher in the range of 100 and 300 ºC and the highest IR shield was 95 % for 200 ºC.

TABLE-1
TRANSMITTANCE IN VISIBLE RAYS BY HEAT TREATMENT TEMPERATURE

Temperature (ºC)		100	200	300	400	500
Transmittance (%)	As-prepared	81.40	77.13	76.75	74.62	73.08
	Coloured	49.04	38.16	31.15	78.04	74.10
	Bleached	81.31	77.05	76.02	78.32	77.08

TABLE-2
TRANSMITTANCE IN ULTRAVIOLET RAYS BY HEAT TREATMENT TEMPERATURE

Temperature (ºC)		100	200	300	400	500
Transmittance (%)	As-prepared	46.87	40.29	38.54	20.23	18.70
	Coloured	50.84	41.99	41.02	23.34	16.68
	Bleached	53.84	45.24	42.21	23.63	20.72

TABLE-3
TRANSMITTANCE IN INFRARED RAY BY HEAT TREATMENT TEMPERATURE

Temperature (ºC)		100	200	300	400	500
Transmittance (%)	As-prepared	47.67	46.33	46.32	67.02	70.03
	Coloured	9.78	5.23	6.67	67.28	37.99
	Bleached	43.92	45.17	44.34	68.89	72.00

Fig. 6 shows the colouration efficiency of WO₃ thin film with heat-treatment variations. The colouration efficiency (η) is defined as optical transmission density [$\Delta OD = \log(T_C / T_C)$] divided by charge density (ΔQ) : η = ΔOD/ΔQ. It indicates how much inserted or extracted ions play a role to change light transmission of the film. Greater colouration efficiency means that small amount of ion insertion or extraction contributes light transmission changes with more efficiency. As is shown in Fig. 7, WO₃ thin film heat-treated at 200 ºC showed the highest colouration efficiency, followed by 100 and 300 ºC. The lowest one is 400 ºC and the next was 500 ºC. The colouration efficiency data confirms that the organic residuals affect the lithium ion intercalation and deintercalation of WO₃ thin film. The heat treatment at 100 ºC is not enough to remove residuals and impurities and that at 300 ºC increased the density and decreased the porosity which decreased the easiness of ion transportation within the film. The crystallization and densification by heat treatment at more than 400 ºC reduces the colouration efficiency greatly, but a little larger efficiency at 500 ºC is considered to result from the decrease of density and crystal phase change.

The optical direct band gap energy variations of WO₃ thin film with heat treatment temperature were calculated by using the following equations.

$$\alpha h\nu = A(h\nu - E_g)^r$$

here α: adsorption coefficient, r : material constant (direct transition material r = 2, indirect transition material r = 1), E_g: band gap energy, h: Planck constant, ν: frequency and A : constant.
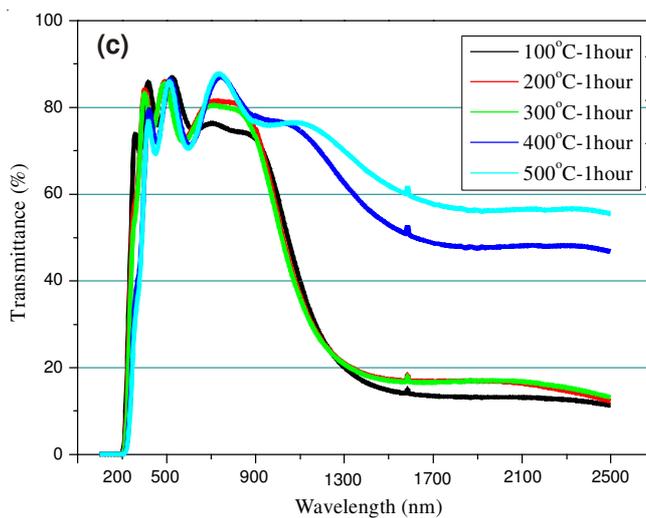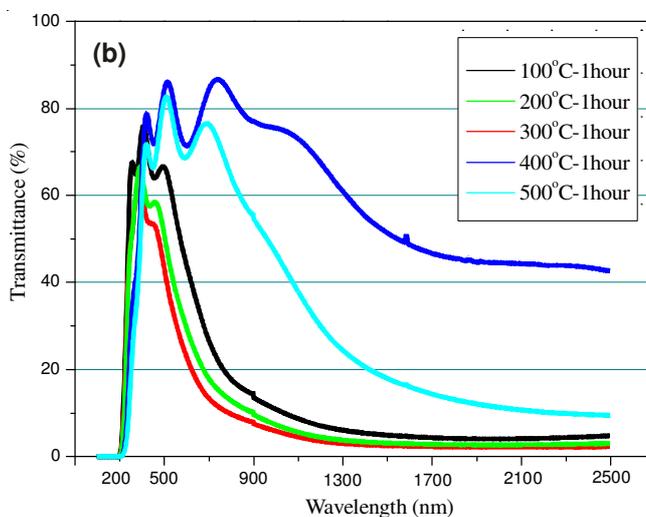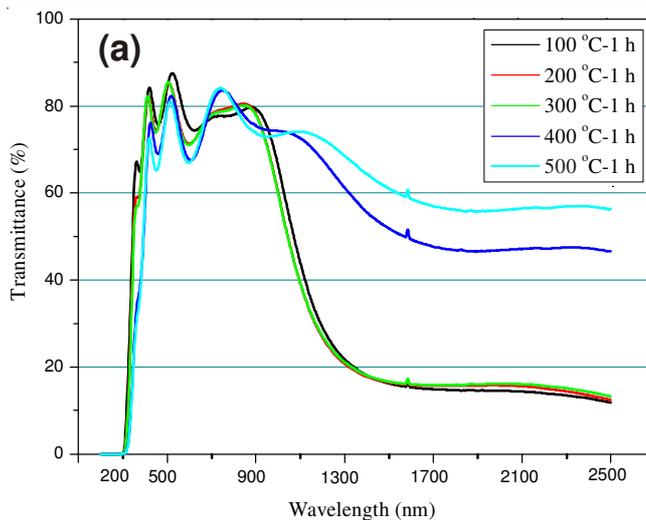

Fig. 6. Transmittance variation by heat treatment temperature (a) as-prepared, (b) coloured and (c) bleached

The optical variations with heat treatment temperature of as-prepared, coloured and bleached state of WO₃ thin film were shown in Fig. 7. Heat-treatment temperature decreased the optical band gap energy. The optical band gap energy widening in amorphous WO₃ thin film is explained by structural trans-

formations from amorphous phase comprized of clusters with hexagonal-like lattice order to monoclinic phase. It is guessed that the band gap of hexagonal phase is larger than that of monoclinic structure. Another explanation for bandgap widening in amorphous phase could be explained by Moss rule, $n^4 E_g \approx$ constant. Here, n is refractive index. A lowering of n by enhanced porosity tends to increase E_g. Our optical bandgap widening could be explained by this Moss rule, which means that amorphous phase of WO$_3$ with higher porosity has larger bandgap energy. After lithium insertion, that is, coloured state, the bandgap energy was larger, which is mostly interpreted in terms of a partial filling of the conduction band. Nakamura and Yamada assigned bandgap widening to the Burstein-Moss effect[2]. However, the bandgap widening by lithium insertion is accompanied by structural changes which can have a significant effect on E_g. After bleaching, the bandgap energy is recovered but not fully, which is considered to result from the remaining of lithium ions partly.
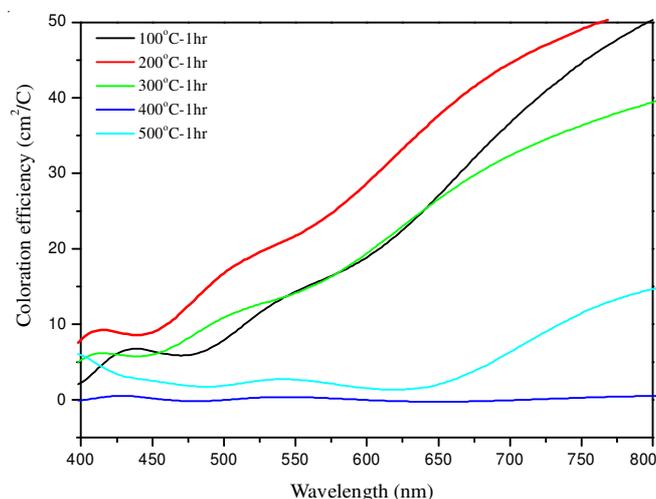

Fig. 7. Colouration efficiency by heat treatment temperature

Conclusion

WO$_3$ thin film was successfully coated by sol-gel coating method and the phase was amorphous below 400 °C and mono-clinic crystal phase was developed at more than 400 °C. The density of the film increased with heat-treatment temperature and the porosity decreased vice versa upto 400 °C. However, the film heat-treated at 500 °C showed a little decrease of density compared to that at 400 °C. The electrochromic properties are related with ion intercalation and deintercaltion like lithium or proton ions. So, it is thought that amorphous or crystalline phase of tungsten oxide is very important for the capability and reversiblility of ion intercalation or deintercalaton. In this study, we analyzed the relationships between heat-treatment temperature and electrochromic properties of tungsten oxide film prepared by sol-gel coating method. It is concluded that amorphous phase shows superior intercalation or deintercalation capability to crystalline phase.

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