

Tungsten oxide film synthesis by spray pyrolysis of peroxotungstic acid and its electrochromic characterization

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Peroxotungstic acid precursor solution was sprayed on indium-doped tin oxide (ITO) glass substrates to synthesize amorphous and crystalline phase tungsten oxide thin films by changing heating temperature. We could synthesize the amorphous phase at below 400 °C and the monoclinic crystalline tungsten oxide at above 400 °C. Electrochemical and in-situ optical transmittance analysis showed that amorphous phase tungsten oxide at 250 °C had a good electrochromic property with a large optical transmittance change between its bleached and colored states. The coloration mechanisms are due to polaron generation by inserting ions and electrons to change W^{+6} state to W^{+5} or W^{+4} state.

Keywords: Peroxotungstic acid, Electrochemical, Electrochromic, Spray pyrolysis, Tungsten oxide

Introduction

Tungsten oxide (WO_3) is a representative cathodic electrochromic material, whose color turns to blue in its reduced state by inserting a proton or lithium ion when a reverse electrical potential is applied and returns to transparent at its oxidized state by extracting ions when a forward electrical potential is applied [1, 2]. There are many research reports about making tungsten oxide film coatings by a sputtering method, pulsed laser ablation deposition method, sol-gel coating method, electrodeposition and spray pyrolysis methods [3-9]. The sputtering method and laser ablation methods offer good quality and homogeneous thin films but their demerits are expensive equipment costs. The sol-gel coating method uses tungsten chloride or peroxotungstic acid as a precursor coating solution and synthesizes tungsten oxide thin films by a dip coating or spin coating methods [10-13]. It is an inexpensive method to obtain amorphous phase in homogeneous tungsten oxide thin films. Another coating method is spray pyrolysis coating method, where a chemical precursor solution is used as in the sol-gel coating method but the difference is the coating method. In the spray pyrolysis method, the precursor coating solution is first sprayed to form mist-like droplets delivered onto substrate at the desired temperature and chemical reaction then occurs on the heated substrate

to result in metal oxide thin film formation.

Several research reports have attempted to obtain tungsten oxide thin films using WCl_6 precursor solution and ammonium tungstate precursor solution [14-16]. However, although many research reports about the sol-gel coating method for tungsten oxide thin film coating using peroxotungstic acid were studied, no attempt has yet been reported to prepare tungsten oxide coatings by a peroxotungstic acid spray coating method. Although peroxotungstic acid has been synthesized for the sol-gel coating of tungsten oxide, researches about the electrochromic tungsten oxide thin film coatings by the spray pyrolysis method using peroxotungstic acid precursor source have not been reported. This study aims to synthesize tungsten oxide thin films by the peroxotungstic acid spray coating method. The peroxotungstic acid is easily synthesized from tungsten metal powder and hydrogen peroxide reactions. In this study, effort was made to obtain the amorphous and the crystalline phases of tungsten oxide by spray coating method and these were characterized in terms of their electrochemical and electrochromic properties.

Experimental

Coating solution synthesis and spray coating

Peroxotungstic acid coating solution was synthesized by reacting tungsten metal powders with 30% hydrogen peroxide at 80 °C and evaporated to remove excess water and hydrogen peroxide at 50 - 60 °C for 4 h. We added 50% ethanol and 50% double distilled water to get 0.01 M peroxotungstic acid spray coating solution. Peroxotungstic acid is known as $WO_3 \cdot nH_2O_2 \cdot mH_2O$, where n was decided

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to be 0.13 by iodimetric titration method in our study. In the case of less than 0.1 of n , peroxotungstic acid precipitates as yellow colloids, which is not adaptable to spray coating.

A normal spray gun with a 0.3 mm diameter nozzle was used to spray coat the solution onto ITO-coated glass substrates on heated plate, where the temperature was controlled from 200 to 400 °C. The carrier gas was nitrogen and the distance between the nozzle and the substrate was 10 cm. Four milliliters of coating solution was sprayed onto 4 cm × 5 cm ITO glass.

Differential thermal analysis and thermogravimetric analysis

The peroxotungstic acid coating solution was dried at 100 °C in dry oven to eliminate solvents for DTA and TG analysis. Dried peroxotungstic acid powder was put into alumina crucibles and alumina standard powder was used as a standard material. Exothermic and endothermic reaction and weight loss or gains were analyzed between room temperature and 600 °C at a ramp rate of 5 °Cmin⁻¹.

X-ray diffraction analysis of tungsten oxide thin film

X-ray diffraction analysis of tungsten oxide thin films was conducted to understand at what temperature the crystalline phase of tungsten oxide was formed. The scan angle range was from 10 to 80 degree and the scan speed was 5 minute degree⁻¹ and the operating voltage was 30 kV and current was 30 mA, and the X-ray target was copper of which wavelength was 1.5405 Å.

Raman scattering spectroscopy

A 532 green laser was used to measure the Raman scattering of the prepared tungsten oxide thin films and the colored state of tungsten oxide by applying -1 V for 30 s. An electrically cooled CCD detector at -75 °C was used to analyze tungsten oxide scattering mode, with a scan time was 30 s for 2 times and the center wave number was 750 cm⁻¹ and a 1800 groove grating was used (JASCO, NRS31000). The optical microscope with a 100 times objective lens was used to observe sample surfaces and measure the scattering.

Electrochemical and electrochromic analysis

The cyclic voltammetric method (CV) and chrono coulometric method (CQ) were used for electrochemical analysis of tungsten oxide films (Autolab, PGASTAT12). The liquid electrolyte was 1 M lithium perchlorate (LiClO₄) dissolved in polycarbonate (PC) solution. Platinum wire was used as a counter electrode and Ag/AgCl was chosen as a reference electrode. For the CV analysis, the tungsten oxide prepared was studied from -1 to +1 V at its scanning speed of 50 mV s⁻¹. For the CQ test, an alternating electrical voltage was applied from -1 V to +1 V for 30 s, respectively, for 10 cycles. A 633 nm wavelength laser and UV/visible light detector were used to evaluate the *in-situ* optical transmittance properties

of spray-coated tungsten oxide thin films.

Results and discussion

The peroxotungstic acid is formed as WO₃· n H₂O₂· m H₂O depending on the synthesis conditions, and the value of n and m can be determined by iodometric titration and TG analysis. The results of TG analysis showed that the weight loss between room temperature and 200 °C was about 12%, 3% between 200 and 300 °C, and 2 % between 300 and 400 °C. Below 200 °C, the weight loss was thought to be due to the decomposition of hydrogen peroxide and the evaporation of water solvent. The two-step weight loss above 200 °C is considered to be from the decomposition of water molecules that were strongly bound to the tungsten oxide. It is known that WO₃ forms via WO₃·H₂O, WO₃·1/2H₂O and WO₃·1/3H₂O. This means that peroxotungstic acid decomposes to tungstic acid (WO₃·H₂O) and lastly forms tungsten oxide between 300 and 400 °C. Two exothermic peaks at 411 and 451 °C show that the amorphous phase tungsten oxide transformed to crystalline phases, which are monoclinic and orthorhombic, respectively [7, 10].

Fig. 1 shows that a monoclinic phase tungsten oxide film was synthesized at 400 °C, and an amorphous phase below 400 °C. Raman spectra of tungsten oxide films, which were spray coated on ITO glass at different temperatures between 200 and 400 °C, are shown in

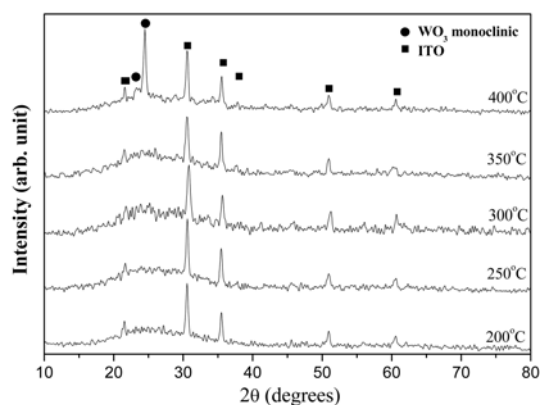


Fig. 1. X-ray diffraction patterns of tungsten oxide thin film on ITO glass formed at various heating temperatures.

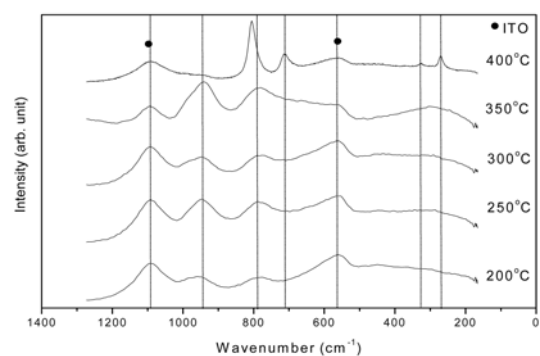


Fig. 2. Raman scattering spectra of as-prepared tungsten oxide formed at various heating temperatures.

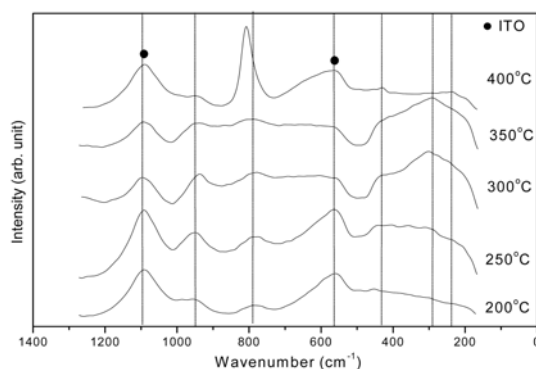


Fig. 3. Raman scattering spectra of colored-state tungsten oxide thin films formed at various heating temperatures. (Coloration was conducted by applying -1 V for 20 s versus Ag/AgCl reference electrode in 1M LiClO₄-PC electrolyte).

Fig. 2 Upto 350 °C, typical amorphous WO₃ features appeared at 785 and 950 cm⁻¹ which were assigned to W-O and W=O stretching modes, respectively. At 400 °C, the characteristic features of monoclinic WO₃ appeared at 268, 711, and 804 cm⁻¹ [6-9]. Fig. 3 shows the Raman scattering spectra of spray-coated tungsten oxide thin films which were colored by applying -1 V for 30 s. In the monoclinic phase tungsten oxide formed at 400 °C, the W-O stretching mode at 804 cm⁻¹ remained in its colored state, but the W-O mode at 711 cm⁻¹ disappeared. The bands at 220, 300 and 440 cm⁻¹ appeared in its colored state, which were assigned to W⁺⁴-O, W⁺⁵-O stretching modes and W⁺⁵=O, respectively. In the amorphous phase tungsten oxide formed below 400 °C, the intensities of bands at 785 and 950 cm⁻¹ changed hardly, but peak intensities at 220, 300, and 440 cm⁻¹ increased. When lithium ions and electrons are inserted into amorphous phase tungsten oxide, the inserted electrons in the W⁺⁵ and W⁺⁴ sites polarize their surrounding lattices to form polarons [6, 7].

The cyclic voltammetry and *in-situ* optical transmittance of spray-coated tungsten oxide thin films are shown in Fig. 4. The cyclic voltammetric curves showed that the reverse electrical voltage inserted lithium ions and electrons into thin films and a forward electrical potential extracted the ions and electrons, of which the maximum peak appeared at around -0.25 V. The tungsten oxide film sprayed at 250 °C showed the maximum curve and CV curve areas decreased with the heating temperature. The reason for a small area CV curve at 200 °C compared to 250 °C is thought to be from impurities in tungsten oxide films, and the decreasing tendency with heating temperature is considered to be due to the densification and crystallization of tungsten oxide thin films. The transmittances of tungsten oxide films at 633 nm were 85% at 200 °C, 75% at 250 °C, 40% at 300 °C, 55% at 350 °C, and 74% at 400 °C. We know that film formation temperature affects transmission of tungsten oxide thin films. When -1 V was applied for coloration, lithium ions were inserted into the tungsten oxide and electrons were

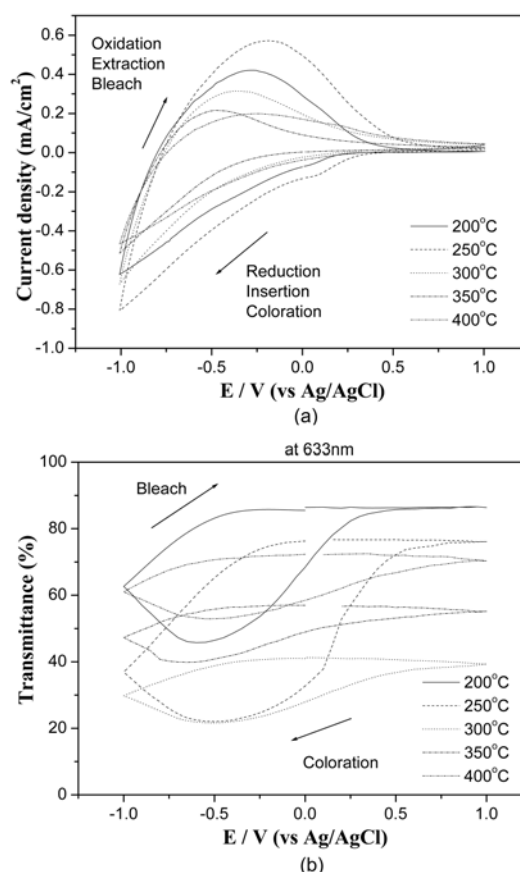


Fig. 4. Cyclic voltammetric curves (a) and in-situ optical transmittance curves of tungsten oxide thin film prepared at different heating temperatures.

also moved into the film, and so a negative current flowed and coloration phenomenon appeared, but this reaction was reversible. The maximum transmittance change was from 75% in the bleached state and 22% in the colored state for the tungsten oxide thin film formed at 250 °C. This tells us that lithium ions more easily diffuse into the amorphous phase tungsten oxide than the crystalline phase. In Fig. 5, the charge density of the tungsten oxide films was 9 mCcm⁻² at 200 °C, 15 mCcm⁻² for the films formed at 250 °C, 11 mCcm⁻² at 300 °C, and 7 mCcm⁻² at 350 and 400 °C. The corresponding optical transmittance changes were 80 to 25% for the films formed at 200 °C, 77 to 20% for 250 °C, 42 to 20 for the films formed at 300 °C, 55 to 37% for the films formed at 350 °C, and 67 to 46% for the films formed at 400 °C. These results show that the same amorphous phase of tungsten oxide had different charge densities or different active ion insertion sites and the amorphous phase prepared at 250 °C had the maximum charge density and showed maximum optical transmittance changes. As expected, the crystalline phase had a small charge density and small optical transmittance change.

Conclusions

We successfully synthesized amorphous and crystalline phase tungsten oxide thin films on ITO glass with a spray

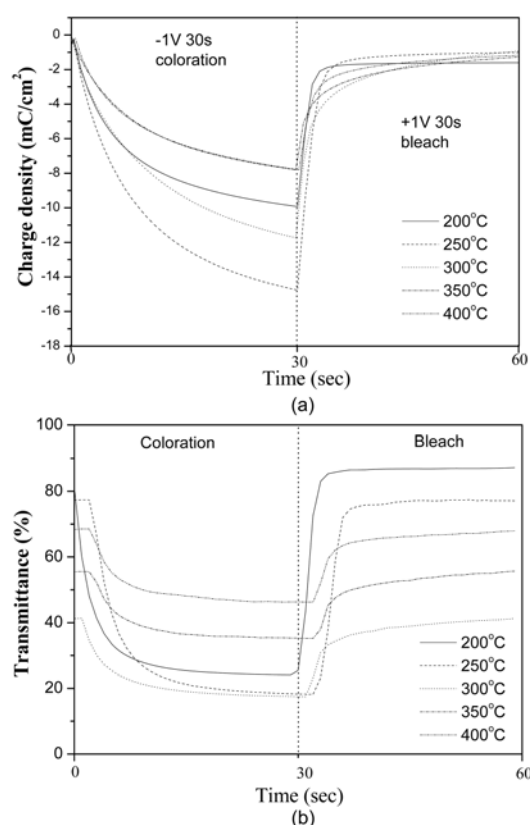


Fig. 5. Chronocoulometric curves (a) and in-situ optical transmittance curves of tungsten oxide thin films prepared at different heating temperatures.

pyrolysis coating of peroxotungstic acid precursor source. Monoclinic phase tungsten oxide forms at 400 °C causes the amorphous phase tungsten oxide to form but the heating below 400 °C forms amorphous phase tungsten oxide. Raman scattering analysis showed that the W^{+6} state turns to W^{+5} and W^{+4} states by the insertion of lithium ions and

electrons into the tungsten oxide thin films. The optimum heating temperature was 250 °C to obtain the highest charge density and the largest optical transmittance changes.

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References

1. S.K. Deb, Appl. Opt. 3 (1969) 192-195.
2. C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, New York, 1995.
3. H.R. Zeller, H.U. Beyler, Appl. Phys. 13 (1977) 231-237.
4. C.G. Granqvist, Electrochimica Acta 44 (1999) 3005-3015.
5. Warren B. Cross, Ivan P. Parkin, and Shane A. O'Neill, Chem. Mater. 15 (2003) 2786-2796.
6. E. Ozkan, S.H. Lee, C.E. Tracy, J.R. Pitts, and S.K. Deb, Solar Energy Materials & Solar Cells, 79 (2003) 439-448.
7. S.H. Lee, M.J. Seong, H.M. Cheong, E. Ozkan, E.C. Tracy, S.K. Deb, Solid State Ionics 156 (2003) 447-452.
8. N.Janke, A. Bieberle, R. Weismann, Thin Solid Films 392 (2001) 134-141.
9. S.H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B.T. To, H. Mahan, Adv. Mater. 18 (2006) 763-766.
10. J.H. Choy, Y.I. Kim, J.B. Yoon and S.H. Choy, J. Mater. Chem, 11 (2001) 1506-1513.
11. K. Yamanka, H. Akamoto, H. Kidou, and T. Kudo, Japanese, J. Appl. Phys. 25 (1986) 1420-1426.
12. A. Cremonesi, D. Bersani, P.P. Lottici, Y. Djaoued, P.V. Ashrit Thin Solid Films, 516 (2008) 4128-4132.
13. C.Y. Kim, J.W. Choi, T.Y. Lim, and D.K. Choi, Key Eng. Mater. 318-318 (2006) 807-810.
14. P.R. Patil, P.S. Patil, Thin Solid Films 382 (2001) 13-22.
15. R. Sivakumar, M. Jyachandran, C. Sanjeeviraja, Mater. Res. Bull 39 (2004) 1479-1489.
16. A. Enesca, C. Enache, A. Duta, J. Schoonman, J. Eur. Ceramic Soc. 26 (2006) 571-576.