Received: November 26, 2018
Revised: December 29, 2018
Accepted: December 30,2018

Sol-Gel derived tungsten oxide thin films deposited by spin coating technique using tungsten powder as starting material

Orawan Thanomkiat[1], Russameeruk Noonuruk[2] and Chokchai Kahattha[3,*]

[1] *Faculty of Science Energy and Environment, King Mongkut's University of Technology North Bangkok Rayong Campus, 21120, Thailand*

[2] *Division of Physics, Faculty of Science and Technology Rajamangala University of Technology Thanyaburi, Thanyaburi, Pathumthani, 12110, Thailand*

[3] *Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, 680 Nittayo Road, Mueang District, Sakon Nakhon, 47000, Thailand*

Abstract

Tungsten oxide (WO_3) thin films were deposited onto F-doped tin oxide (FTO) substrates using spin coating technique. The starting precursor for tungsten source was prepared from tungsten powder (Aldrich 12 micron; 99.9%) dissolved in 15% hydrogen peroxide. The coated films were annealed in ambient air for 2 hours at different annealing temperatures ranging from 200-500 °C. The differential-thermogravimetric measurement on the starting stock solution was performed to study its thermal property and decomposition/transformation. It was informed that the phase transformation and tungsten oxide crystallization was initiated at the temperature beyond 300 °C. X-ray diffraction was employed to characterize structural properties of the prepared films. The relevant chemical bonding of the films was investigated by fourier transform infrared spectroscopy. The optical and electrochromic properties of thin films were monitored by mean of UV-Vis spectroscopy technique. Further results and discussed will be represented in details.

Keywords: Sol-gel, tungten oxide, spin coating, annealing temperature

1. Introduction

Due to its outstanding optical properties, tungsten oxide (WO_3) is one of the most extensively used materials for practical application such as smart windows, electrochromic windows, switchable devices and sensors [1]. In particular, tungsten oxide has been widely applied as a key active material for smart windows, which possess variable light transmission characteristics and may be useful for applications in building or car industries. Up to now, several techniques have been notified to be applicable for metal-oxide thin film coatings including sputtering [2], chemical vapor deposition [3], electron beam deposition [4], pulsed spray pyrolysis [5] and spin coating [6]. Sol-gel spin coating has significant advantages among the other including cost-effective experimental arrangement, ease of adding dopant, high homogeneity, low process temperature, reproducibility and mass production capability for uniform large area coatings, Meanwhile, many effort have been devoted to improve the optical properties of tungsten oxide films by doping with transition metals such as Ti, V, Co, Fe, Zn [7]. Nevertheless, based on our recent knowledge a limitation of literatures focusing on the preparation and characterization of WO_3 thin films are available. In this work, WO_3 optical thin films were coated onto F-doped SnO_2 (FTO) substrates by spin coating technique. The structural properties of WO_3 thin films were characterized by X-ray diffraction technique (XRD). The relevant optical properties (color or bleach) were extracted from transmission spectra obtained by UV-vis spectroscopy.

Corresponding Author E-mail: kahattha@gmail.com

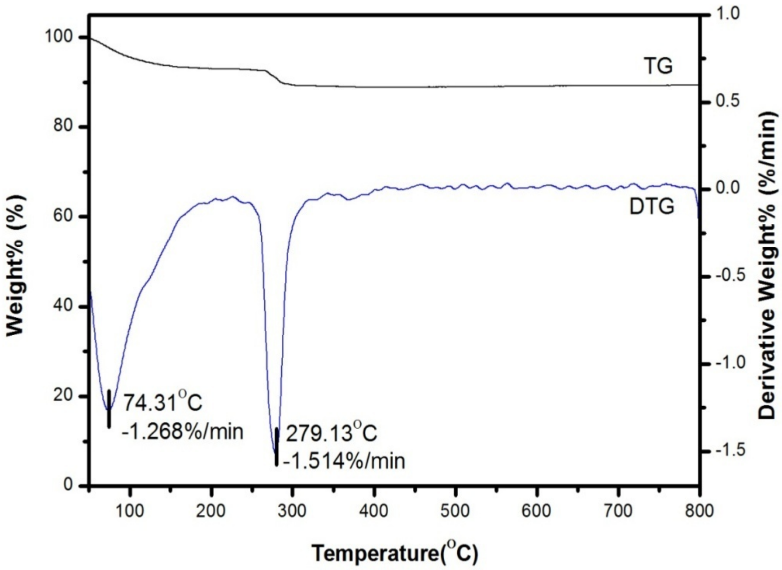

Fig. 1. TG-DTA curves of as-prepared WO_3 powder

2. Experimental details

The WO_3 thin films were deposited by sol-gel spin coating. The starting precursor was prepared from tungsten powder (Aldrich 12 micron; 99.9%) dissolved in 15% hydrogen peroxide. The dissolution was kept at 10-15 °C which finally resulted to pale yellow solution. WO_3 electrochromic thin films were deposited onto FTO (thickness~400 nm) conducting substrates with sheet resistance of 15 Ω/m. The sol-gel solution was coated by a spinner at frequency of 2000 rpm. After each coating, the sample was baked at 100 °C for 5 min and finally annealed at different temperatures from 200-500 °C in ambient air for 2 h. The effect of annealing temperature on structural properties of the films were characterized by X-ray diffraction (XRD). The optical properties of the films were investigated using UV-Vis spectrophotometer (Thermo Electron Corporation Heliosα).

3. Results and discussion

The differential-thermogravimetric (TG/DTG) curves of tungsten powder stock solution were carried and the corresponding result is illustrated in Fig. 1. The first shown slight weight loss at temperature 74 °C attributes to evaporation of physically-adsorbed water and molecules, decomposition of peroxo groups and the combustion of organic species. The second peak at 280 °C is ascribed to burn out of organic species which starting point of crystallization of WO_3 [8].

The X-ray diffraction patterns of WO_3 thin films with difference annealing temperatures on FTO substrates are illustrated in Fig.2. The XRD patterns of the films annealed at 200 and 300 °C do not exhibit characteristic peaks of WO_3, indicating that the structure of the films deposited at this temperature are amorphous phase. With increasing deposition temperature elevated to 400 °C, the noticeable diffraction peak position at 2θ values of 24.14° corresponding to (200) orientation plane of monoclinic WO_3 is clearly observed, indicating

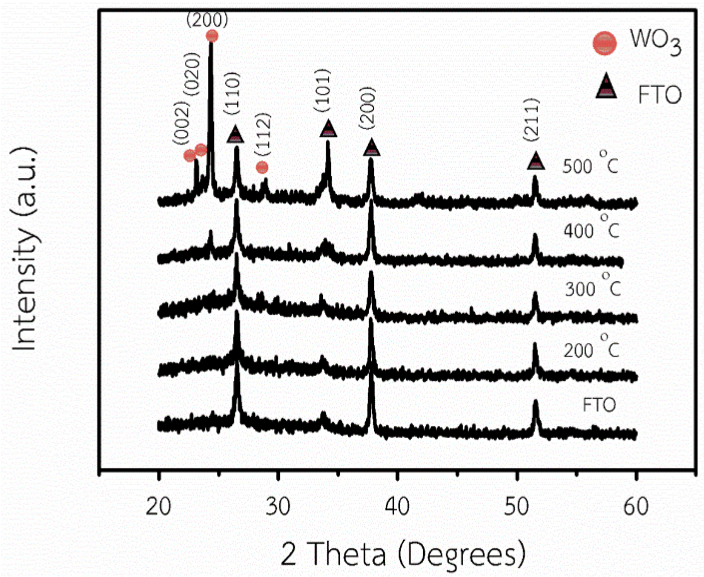

Fig. 2. XRD patterns of WO_3 thin films annealed at different temperatures.

the formation of monoclinic structure of WO_3 films after annealing process. Further increasing temperature to 500 °C results to the intensity of the WO_3 (200) peak becomes stronger and the existence of (002) orientation plane peak at 2θ values of 23.1° which reflect to as annealing temperature arise suggesting that crystallinity of the film significantly improves at higher annealing temperature. The other diffraction peaks identified at 26.5°, 33.7°, 37.7°, 51.5° correspond to (110), (101), (200), (211) orientation plane for FTO substrate [9]. With increasing deposition temperature elevated to 500 °C observed in XRD patterns at 2θ=24.14° and 28.64° planes (002), (020), (200), (112) indicating peak of WO_3 [10].

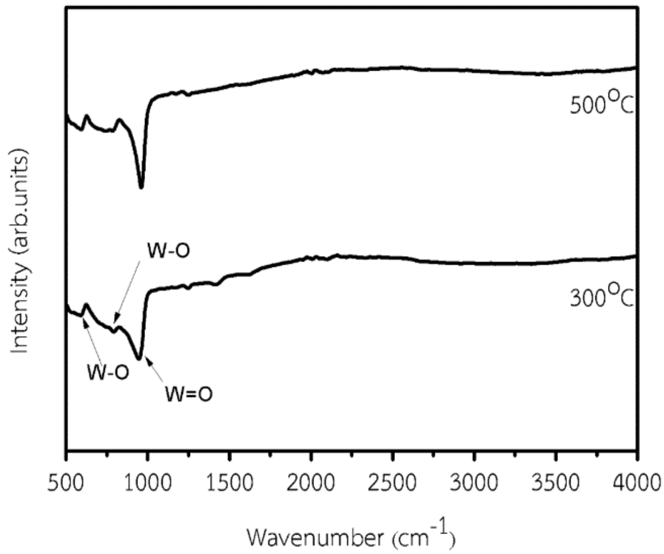

Fig. 3. FTIR spectra of WO3 thin films with annealing temperature at 300 °C and 500 °C.

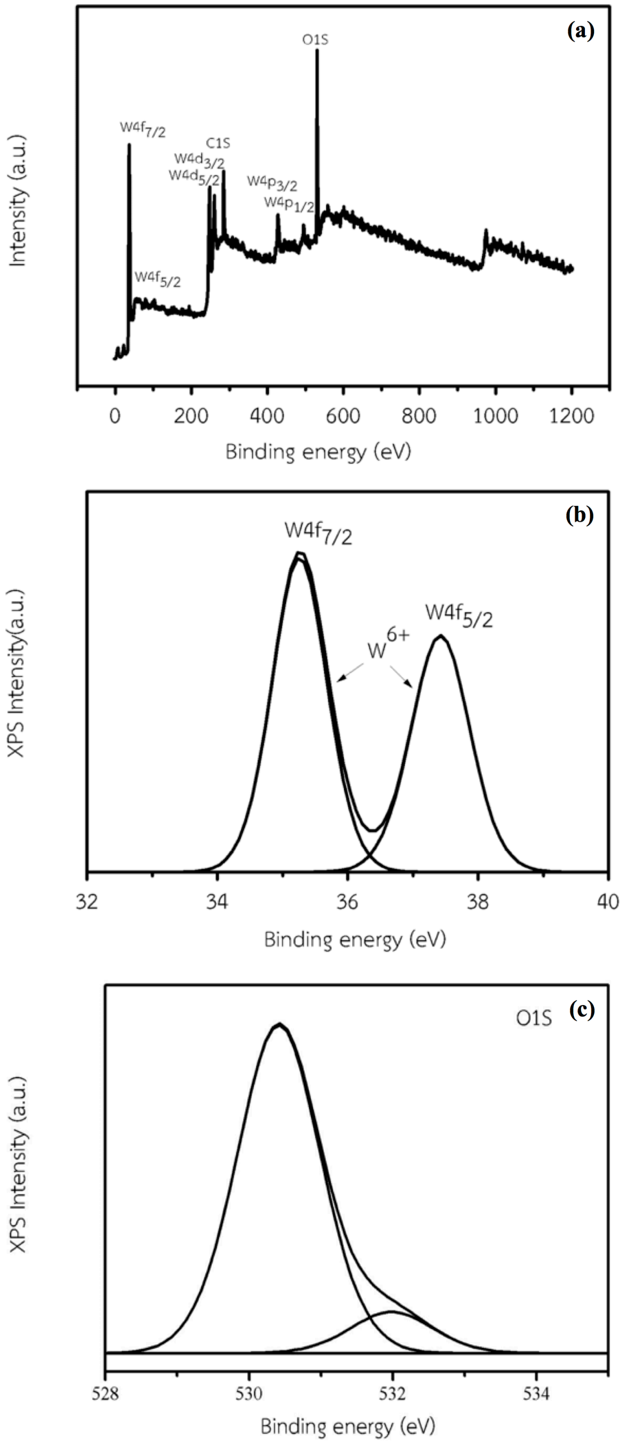

Fig. 4. High resolution X-ray photoelectron of WO_3 thin films annealed at 500 °C: (a) survey, (b) W4f, (c) O1s

The vibrational modes of the chemical groups in the WO_3 at different temperature were examined by FTIR spectroscopy. Fig. 3 shows the FTIR spectra of WO_3 thin films with different annealing temperatures at 300 °C and 500 °C in in the wavelength range 500-4000 cm^{-1}. The film with annealing temperature at 300 °C shows the peaks situate at 661, 797 and 948 cm^{-1} are ascribed to the vibration bonding of W-O, W-O and W=O stretching mode, respectively. In addition, the intensity of W=O bonding significantly increased when annealing temperature raised to 500 °C. This result implies that the number of W=O increases with the annealing temperature [12]. XRD and FTIR results indicate that the annealing temperature can be improved the quality of the films.

The survey spectrum of XPS shows three peaks corresponding to tungsten, oxygen and carbon based in the binding energy range 0-1200 eV, as shown in Fig. 4a. The fine spectrum of W consisting of spilt double peaks is shown in Fig. 4b. Two major peaks are well separated without any shoulders at ca. 35.6 and 37.6 eV are ascribed to $W4f_{7/2}$ and $W4f_{5/2}$, respectively. This result suggests that the W^{6+} ions are obtained on the surface of a film. The O1s peaks at 530.17 and 532.15 eV are assigned to the O^{2-} and O-H phases at the surface of WO_3 thin films (as shows in Fig. 4c) [13].

The electrochromic experiment of WO_3 films prepared by spin coating method using H_2SO_4 concentration of 0.01 M as an electrolyte. Electric field + 3V for 30 s. The light transmission of three states consist of as-deposited state, color state and bleach state are shown in Fig. 5. From the results, the as-deposited film shows the highest transmittance. After applied electric field, the film are obtained to dark-blue color at colored state owning to the ion insertion reduced some W^{6+} states to W^{5+} states. On the contrary, the ions ejection reduced some W^{5+} states to W^{6+} states lead to the film change from colored to bleach state. The ions transport process according to the following electrochemical reaction [14]:

$$WO_3 + xH^+ + xe^- \leftrightarrow H_xWO_3 \tag{1}$$

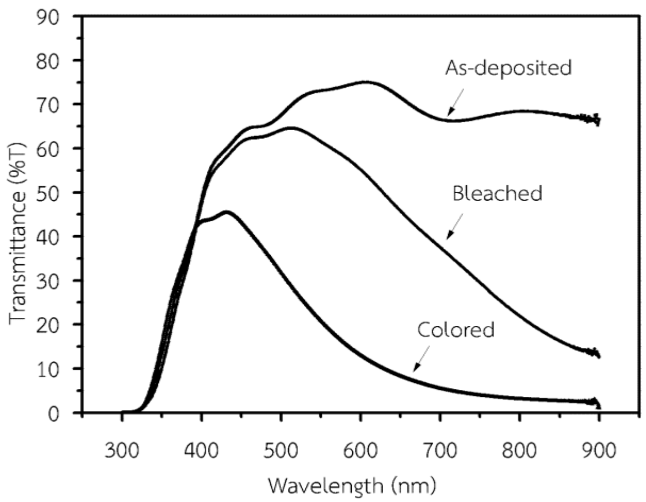

Fig. 5. Transmittance spectra of WO3 thin films annealed at 500 °C with different colored states.

4. Conclusion

In summary, the WO_3 films with monoclinic structure were successfully deposited via sol-gel spin coating technique using annealing temperature at 500 °C. FTIR spectra results show the peaks of W-O and W=O stretching mode. The XPS results indicate that the W^{6+} ions are obtained on the surface of a film. The electrochromic result suggests that the colored state of WO_3 films can be transformed by injection/ejection of ions into the films which suitably as smart window.

Acknowledgement

This work has been partially supported by Sakon Nakhon Rajabhat University (SNRU) and King Mongkut's University of Technology North Bangkok. Authors would like to express deep thank to Technology Rajamangala University of Technology Thanyaburi for experimental support.

References

[1] Georg A. Switchable windows with tungsten oxide. Vacuum. 2008;82(7):730-735.
[2] Karuppasamy A. Studies on electrochromic smart windows based on titanium doped WO_3 thin films. Thin. Solid. Films. 2007;516(2-4):175-178.
[3] Garga D. An economic analysis of the deposition of electrochromic WO_3 via sputtering or plasma enhanced chemical vapor deposition. Mat. Sci. Eng B-Solid. 2005;119(3):224-231.
[4] Joraid AA. Comparison of electrochromic amorphous and crystalline electron beam deposited WO_3 thin films. Curr. Appl. Phys. 2009;9(1):73-79.
[5] Patil PS. Electrochromic properties of spray deposited TiO_2-doped WO_3 thin films. Appl. Surf. Sci. 2005;250(1-4):117-123.
[6] Isik D. Structural, electrochemical and optical comparisons of tungsten oxide coatings derived from tungsten powder-based sols. Thin. Solid. Films. 2009;518(1):104-111.
[7] Suvarna SR. Titanium doping effects in electrochromic pulsed spray pyrolyzed WO_3 thin films. Solid. State. Ionics. 2008:179(9-10):314-323.
[8] Deepa M, Saxena TK, Singh DP, Sood KN, Agnihotry SA. Spin coated versus dip coated electrochromic tungsten oxide films: Structure, morphology, optical and electrochemical properties. Electrochim. Acta. 2006;51(10):1974-1989.
[9] Shankar VV, Martin H, Alan S, Kirill S, Dennis K, Radim B, Wolfgang S. Alfred L. Enhanced photoelectrochemical properties of WO_3 thin films fabricated by reactive magnetron sputtering. Int. J. Hydrogen. Energ. 2011;36(8):4724-4731.
[10] Ahn KS, Lee SH, Dillon AC, Tracy CE, Pitts R. The effect of thermal annealing on photoelectrochemical responses of WO_3 thin films. J. Appl. Phys. 2007;101(9):093524.
[11] Cremonesi A, Bersani D, Lottici PP, Djaoued Y, Ashrit PV. WO_3 thin films by sol–gel for electrochromic applications. J. Non-Cryst. Solids. 2004;345&346:500-504.
[12] Abbas F, Bensaha R, Tarore H. Effect of Hg^{2+} doping of the annealing temperature on the nanostructural properties of TiO_2 thin films obtained by sol–gel method. C. R. Chimie. 2014;17(12):1176–1183.
[13] Bathe SR, Patil PS. Infiuence of Nd doping on the electrochromic properties of WO_3 films. J. Phys. D Appl. Phys. 2007;40(23):7423-7431.
[14] Shinde PA, Lokhande AC, Patil AM, Lokhande CD. Facile synthesis of self-assembled WO_3 nanorods for high-performance electrochemical capacitor. J. Alloy. Compd. 2019;770:1130-1137.