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Preparation and characterization of electrochromic tungsten oxide–titania composite thin films with different tungsten/titanium ratios

Cheng-Lan Lin [a,b,*], Yan-Wen Chen [a], En Chen [a]

[a] Department of Chemical and Materials Engineering, Tamkang University, New Taipei City 25137, Taiwan
[b] The Energy and Opto-Electronic Materials Research Center, Tamkang University, New Taipei City 25137, Taiwan

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ABSTRACT

Tungsten oxide–titania composite thin films with different W/Ti atomic ratios were prepared and characterized in this study. Surface morphology, composition and structure of the composite thin films were investigated by scanning electron microscope with an energy dispersive spectrometer, X-ray diffraction and atomic force microscope analyses. Electrochromic properties including transmittance modulation ability, coloration efficiency and coloring/bleaching response time of these thin films were examined using cyclic voltammetry and double-potential-step experiment with in-situ ultraviolet–visible spectroscopy measurement. The presence of titania in the composite thin film could inhibit the crystal growth of tungsten oxide, which enhances the transmittance modulation ability and coloration efficiency but prolongs the coloring/bleaching response time of the composite thin film. The tungsten oxide–titania composite thin film (WTi-30) with a W/Ti atomic ratio of 78/22 exhibited better transmittance modulation ability (57.5%) and coloration efficiency (49.2 cm^2/C) than a pristine tungsten trioxide thin film (53.6%, 36.2 cm^2/C).

1. Introduction

An electrochromic (EC) material is the one that can change its optical property reversibly upon being electrochemically oxidized or reduced, and such material finds its potential applications in automotive glass, skylight, motorcycle helmet or ski goggles [1,2]. Tungsten trioxide (WO_3) is a well-known EC material with stable chemical as well as electrochemical properties and has been studied extensively [2–4]. WO_3 thin film is a cathodically coloring EC material which changes from its bleached (colorless) state to colored (blue) state during reduction reaction, and can be oxidized back to its bleached state reversibly. The insertion or de-insertion of electrons and cations, such as H^+ or Li^+, into or out of a WO_3 thin film take place during its redox process and which can be expressed as follows: [4]

$$WO_3(\text{colorless}) + xLi^+ + xe^- \leftrightarrows Li_xWO_3(\text{blue}). \quad (1)$$

WO_3 thin films have been synthesized using diverse techniques such as reactive DC magnetron sputtering [5], spray pyrolysis [6], thermal evaporation [7], chemical vapor deposition [8–11], hydrothermal method [12,13] or sol–gel method [14–28] etc. Among these methods, sol–gel method has the advantages of good control over microstructure and composition of the resulting film and low reaction temperature, and was employed to prepare the tungsten oxide–titania composite thin films in this study. Peroxotungstic acid (PTA) [14–20] or acetylated peroxotungstic acid [21–23] is the most commonly used precursor while using sol–gel method to prepare a WO_3 thin film. The precursor sol solution can be either spin-coated or dip-coated onto a conducting substrate and then followed by heat treatment to form a WO_3 thin film. Additives such as polyethylene glycol [23–25] or metal dopants [26–28] have been introduced into the sol solution to improve the electrochromic performance of the resulting WO_3 thin film. Some attempts of incorporating titania into various tungsten oxide structures have also been made to obtain tungsten oxide–titania composite materials, and their photocatalytic properties [29–31] or electrochromic properties [32–38] were investigated. Z. Wang and X. Hu [32] prepared TiO_2 (10 at.%)-doped WO_3 thin film by adding titanium tetra-n-butoxide into PTA aqueous sol solution, and suggested that the electrochromic property of the composite thin film is closely related to its water content. K. Paipitak et al. [34] studied the electrochromic performances of Ti(5, 15 and 20 wt.%)-doped WO_3 thin films, and find that the transmittance modulation ability of a WO_3 thin film with 5 wt.% Ti doping can be enhanced. E. O. Zayim et al. [33] synthesized TiO_2(1, 5, 10 and 15 mol%)-mixed WO_3 thin films, and suggested that the electrochromic properties of the thin films were improved due to the amorphous structure preserved by Ti addition. J. Göttsche et al. [38] synthesized the mixed WO_3–TiO_2 thin films with Ti/(Ti + W) mol% up to

* Corresponding author at: Department of Chemical and Materials Engineering, Tamkang University, New Taipei City 25137, Taiwan. Tel.: +886 2 26215656x2723; fax: +886 2 26209887.
E-mail address: cllin@mail.tku.edu.tw (C.-L. Lin).

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50 by sol–gel method, and the coloration efficiency decreased as the Ti content in the film increased.

Many of the studies were concentrated on the Ti-doped WO_3 thin films with Ti content lower than 20 mol%, but few were focused on the electrochromic performances, especially the coloring/bleaching response time, of ones with higher Ti loading. In this study, tungsten oxide–titania composite thin films with different W/Ti atomic ratios ranging from 100/0 to 50/50 were synthesized on fluorine-doped tin oxide (FTO) conducting glass by sol–gel method with spin-coating technique, and the effects of W/Ti atomic ratios on the physical, optical, electrochemical and electrochromic properties of these composite thin films were investigated.

2. Experimental details

Tungsten powder (12 μm diameter), propylene carbonate (PC) and titanium tetra-n-butoxide (TTNB) were purchased from Acros. Hydrogen peroxide (35%) and ethanol (99.5%) were obtained from Shimakyu's pure chemical. FTO conducting glasses (6–8 Ω/square, thickness = 2.2 mm) were acquired from Hartford glass Co., Ltd. The FTO conducting glasses were sonicated in deionized water and acetone sequentially, washed in a boiling ethanol bath for 15 min then stored in air before use. For the preparation of PTA powder, 6 g of tungsten powder was slowly added into 50 mL of 35% H_2O_2 solution in an ice bath with continuous magnetic stirring, and then stored at room temperature for 24 h till the tungsten powder was completely dissolved. A platinum black plate was dipped into the solution for 20 h to decompose the excess H_2O_2, and the solution was rotary-evaporated to yield yellow PTA powder.

For the preparation of a WO_3 thin film, the above PTA powder was added into 45 mL dry ethanol and was stirred for 3 h then filtrated to obtain a yellowish transparent PTA solution. The PTA solution was spin-coated onto a FTO conducting glass (spin rate = 3000 rpm, 60 s) and then annealed at 200 °C in air for 3 h to obtain a colorless transparent WO_3 thin film. For the preparation of tungsten oxide–titania thin films, the desired amount of TTNB was added into ice-cooled PTA solutions and magnetically stirred for 20 min to give sol solutions with different W/Ti atomic ratios of 90/10, 80/20, 70/30, 60/40 and 50/50. The sol solutions with W/Ti ratios of 90/10, 80/20 and 70/30 were transparent and gradually changed from yellow into orangish-red under stirring, indicating the formation of titanium peroxo complexes with O_2^{2-} acting as bidentate chelating ligands. Yellowish colloid-like solution was formed when the W/Ti ratio was 60/40 or 50/50, which might corresponding to presence of titania nanoparticles in the sol solution. The sol solutions were spin-coated onto FTO conducting glasses following the same procedures describe above, and colorless transparent tungsten oxide–titania composite thin films on FTO conducting glasses were obtained after the annealing process.

The structure and surface morphology of the composite thin films were investigated by X-ray diffraction (XRD, Bruker, D8A) using Cu-Kα radiation at 40 kV and 40 mA and scanning electron microscope (SEM, Carl Zeiss, Leo 1530) with an energy dispersive spectrometer (EDS) at an operating voltage of 15 kV. The thicknesses of the thin films were measured by a surface profilometer (Kosaka Laboratory Ltd., ET3000). Atomic force microscopy (AFM) using multi-mode scanning probe model with a nanoscope IV controller by Digital Instruments Inc. (Veeco) was used to observe the surface morphology and roughness of the thin films at ambient condition. Electrochemical experiments were performed in a conventional three-electrode system with a potentiostat/galvanostst (CH Instrument, CHI-760D). The reference electrode was an Ag/AgCl reference electrode and all the potentials reported in this work have been measured versus it. A platinum coil was used as the counter electrode and the electrolyte was a PC solution containing 1.0 M $LiClO_4$ as the supporting electrolyte. An UV/Vis spectrophotometer (Unicam, UV500) was employed to record in-situ the absorbance or transmittance changes during the electrochemical redox reactions of a composite thin film.

3. Results and discussion

The tungsten oxide–titania composite thin films were prepared via sol–gel method in this study. The sol solutions were obtained by mixing PTA and TTNB using dry ethanol as the solvent. The PTA/TTNB sol solutions were spin-coated onto FTO conducting glasses followed by annealing at 200 °C in air for 3 h, and colorless transparent composite thin films with various W/Ti atomic ratios were then obtained. The W/Ti atomic ratios were controlled by the relative amount of PTA and TTNB used in the sol solutions to be 90/10, 80/20, 70/30, 60/40 and 50/50, and the resulting tungsten oxide–titania composite thin films were named as WTi-10, WTi-20, WTi-30, WTi-40 and WTi-50, respectively. A WO_3 thin film obtained from pure PTA sol solution was also prepared for comparison.

3.1. Structure and surface compositions

SEM images of the as-prepared tungsten oxide–titania composite thin films are shown in Fig. 1. Agglomerates and small cracks were observed on the surfaces of the WTi-10 and WTi-20 composite thin films. In contrast, WTi-30, WTi-40 and WTi-50 composite thin films showed smooth surface morphology, and which suggested that the tungsten and titanium moieties might have been well mixed in these composite thin films. It is deduced that the introduction of titanium moieties into tungsten oxide thin film can prevent the formation of cracks during the annealing process.

A surface profilometer was used to measure the thicknesses of the thin films and the results are listed in Table 1. The average thickness of the pristine WO_3 thin film was 248 nm. The tungsten oxide–titania composite thin film became thicker as the amount of titania in the composite thin film increased (from 284 nm for the WTi-30 composite thin film to 367 nm for the WTi-50 composite thin film). Surface compositions of the tungsten oxide–titania composite thin films were investigated by EDS and the results are listed in Table 1. The results are average values from at least three individual measurements. Except for the WTi-10 composite thin film, the W/Ti ratios in the tungsten oxide–titania composite thin films are higher than the designed values (in the sol solution), and the exact reason for such discrepancy is under investigation.

In order to investigate the effects of titania to the structure of a tungsten oxide thin film, WO_3 and WTi-30 composite thin films which annealed at 200, 300, 400 or 500 °C were prepared and analyzed using XRD, and the results are shown in Fig. 2. For the pristine WO_3 thin film, distinct diffraction peaks corresponding to the monolinic crystalline system of WO_3 appeared (Fig. 2(a)) if the annealing temperature is higher than 300 °C. On the other hand, there was no apparent diffraction peak that could be observed for the WTi-30 composite thin film, and even an annealing temperature of 500 °C was used. The above results suggested that the incorporation of titania might inhibit the crystal growth of the tungsten trioxide during the annealing process. It is known that WO_3 thin films containing amorphous phases [21,22] or microstructures [33] have better coloration efficiency than the one with compact crystalline structure, and therefore the effects of titania on the electrochromic performance of the tungsten oxide–titania thin film were then investigated.

3.2. UV–Vis spectra and electrochemical properties

The transmittance spectra of a pristine WO_3 thin film and the tungsten oxide–titania composite thin films are shown in Fig. 3. The colored-state or bleached-state of the thin films was achieved by applying a constant potential of −1.0 V or 1.0 V, respectively, and the corresponding transmittance spectra were recorded after 120 s with the potential