

EFFECT OF TITANIUM DOPANT ON PHYSICAL AND OPTICAL PROPERTIES OF WO₃ THIN FILMS PREPARED BY SOL-GEL METHOD

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Abstract

In this present work, the influence of incorporated Ti dopants on the physical and optical properties of WO₃ sol-gel derived thin films are investigated and represented. Ti-doped WO₃ thin films with different Ti doping contents (5 wt%, 10 wt%, and 20 wt%) are fabricated on F-doped tin oxide substrates using the spin coating technique. Tungsten powders and titanium butoxide are used as starting sources of the W and Ti ions, respectively. After the coating process, as-deposited films are annealed at 500°C for 2 h in ambient air. The effects of the dopant on the crystal structure, surface morphologies, chemical bonding, and optical properties of the films are investigated by the X-ray diffraction technique (XRD), scanning electron microscopy, Fourier transform infrared (FTIR), and ultraviolet-visible spectrophotometry. The XRD results indicate the monoclinic structure of the prepared films with a significant alteration in the crystalline size when the film was incorporated with the Ti dopant. The FTIR results reveal the deterioration in the W and O bonding as the film is doped with the Ti dopant. The optical band gaps of the films exhibit a significant blue shift with increasing the Ti doping content. The optical density change and cyclic voltammetry results indicate that the performance of WO₃ film applied as a smart window or energy storage can be enhanced by doping with Ti ions.

Keywords: Titanium dopant, physical and optical properties, WO₃, sol-gel method

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Introduction

In recent years, tungsten trioxide (WO₃)-based materials have attracted considerable attention owing to their excellent optical reversibility from transparency to dark blue induced by an electrochemical process, leading them to potential applications in electrochromic windows, optical switchable devices, and energy storage materials (Nwanya *et al.*, 2014). Furthermore, many techniques have been employed to improve these performances such as combining with other materials (Figueiredo *et al.*, 2015) and doping with other elements (Boudiba *et al.*, 2011). Consequently, doping with various elements such as Ti, Nb, Ru, Fe, Mo, and Ni has been selected as a promising enhancement of the electrochromic properties of WO₃ since it can promote the carrier ions leading to the improvement of the exchange rate of electrons between the dopant and the host (Mukherjee and Sahay, 2016). Among suitable transition metal ions, titanium (Ti) is considered as an effective doping element into the WO₃ structure due to the close ionic radius between the Ti and W elements (Bathe and Patil, 2008). Recently, numerous research groups have concentrated on effective techniques for preparing suitable element-doped WO₃ such as sputtering, chemical vapor deposition, hydrothermal processing, and sol-gel processing. Among these techniques, the sol-gel process is well suited for the preparation of these materials because of its simplicity, low equipment cost, ease of operation without a vacuum system, comfort for doping with other elements, and the ability to be coated on a large area window.

In this work, we focus on the simple preparation of Ti-doped WO₃ films by the sol-gel spin coating process. The effects of the titanium doping content on the crucial physical and optical properties of the films were thoroughly studied.

Materials and Methods

Ti-doped WO₃ films with various titanium contents were prepared by a sol-gel spin

coating method. Tungsten powder (Aldrich 12 micron 99.9%) and titanium butoxide (Ti(C₄H₉O)₄) (Aldrich 1.00 g/ml 97%) were used as starting source materials for the W and Ti, respectively. In the typical preparation, 1 g of tungsten powder was dissolved into 10 ml of 15% hydrogen peroxide and maintained at 10-15°C for 1 h. The transparent solution was obtained after the complete dissolving process. In addition, 40 ml of absolute ethanol and 0.058 ml of titanium butoxide (for 5 wt% doping) were subsequently added into the stock solution and then continuously stirred for 2 h at room temperature in ambient air. Fluorine-doped tin oxide (FTO) glass with dimensions of 2.0×2.0 cm² and a sheet resistance of 15 Ω/□ was used as the transparent conducting substrate of the Ti-doped WO₃ films. The spin coating process was performed at room temperature with a 2-step spin speed of 500 rpm for 10 s and 2,000 rpm for 20 s. The films were baked at 100°C for 5 min and annealed at 500°C for 2 h under ambient air. The crystalline structure and phase identification of the films were investigated by the X-ray diffraction technique with a monochromatic source of Cu K_α (λ = 0.15405 nm) using a MiniFlex model (Rigaku Corporation, Tokyo, Japan). The surface morphology and chemical bonding were characterized with a field-emission scanning electron microscope, model S-4700 FE-SEM, (Hitachi Ltd., Tokyo, Japan) with an accelerating voltage at 5.0 kV and Fourier transform infrared spectroscopy spectrometer, model Nicolet 6700 FT-IR, (Thermo Fisher Scientific, Waltham, PA, USA), respectively. The transmittance spectra were obtained with a UV-Vis spectrophotometer Thermo Electron Corporation Helios α model (Thermo Fisher Scientific, Waltham, PA, USA) in the wavelength of 300-900 nm. The colored-bleached state measurements of the films were carried out in 0.001 M of H₂SO₄ solution with an applied voltage of 1 V for 5 s. Cyclic voltammetry (CV) was employed to characterize the electrochromic properties of the samples with 0.01 M of H₂SO₄ solution as the electrolyte

in a 3-electrode cell system using Ag/AgCl as the reference electrode and Pt wire as the counter electrode in the range of -1.0 V to +1.0 V at a scan rate of 50 mV/s.

Results and Discussion

The structural properties of the Ti-doped WO₃ thin films and the FTO substrate are illustrated by the XRD patterns (Figure 1). From our previous XRD results, all samples show the characteristic diffraction peaks of the FTO and the diffraction peaks are observed at $2\theta = 23.1^\circ$, 24.14° , and 28.64° which corresponded to the (002), (200), and (112) orientation planes of the monoclinic structure of WO₃ (JCPDS file No. 83-0950). No characteristic peaks attributed to titanium oxide are detected, indicating that the Ti ions can properly be doped into the WO₃ lattice and may be attributed to the incorporation of a smaller ionic radius of Ti⁴⁺ (0.60 Å) into the WO₃ lattice and substituted to the W⁶⁺ (0.62 Å) situation due to its close ionic radius (Bathe and Patil, 2008). In addition, the disappearance of the (002) and (112) orientation planes and the decrease of the intensity of the (200) plane is observed with increasing the Ti doping content. This phenomenon indicates that the crystalline growth process can be

obstructed by the interstitial Ti⁴⁺ ions leading to the deterioration of the prominent orientation plane in WO₃ (Cai *et al.*, 2017).

The interplanar spacing (*d*-spacing) and grain size of Ti-doped WO₃ thin films could be calculated by Bragg's law and Scherrer's equation, respectively (Figure 2). The increase in the calculated *d*-spacing with increasing the Ti doping contents may be ascribed to its closed ionic radius (Ti⁴⁺ and W⁶⁺) leading to the interstitial or substitution of Ti⁴⁺ into the WO₃ structure (Bathe and Patil, 2008). On the contrary, the diminishing of the grain size with increasing the Ti doping contents may be attributed to the integration of Ti⁴⁺ ions in the grain boundaries of the WO₃ grains. Consequently, the grain growth process of WO₃ is obstructed by the interstitial Ti⁴⁺ ions leading to a significant grain size decrease of the WO₃ (Cai *et al.*, 2017). In addition, from Scherrer's equation, the calculated grain size can be reduced by increasing the full width at half maximum.

Figure 3 demonstrates the SEM images of the undoped and Ti-doped WO₃ thin films prepared by the sol-gel spin coating method and annealed at 500°C for 2 h. From the SEM images' results, it is clearly shown that Ti-doped WO₃ thin films with a high density grain size of about 20 nm can be produced by

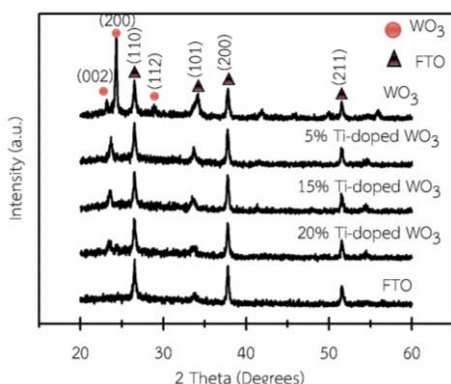


Figure 1. XRD patterns of Ti-doped WO₃ thin films with various Ti doping contents prepared by the sol-gel spin coating method and annealed at 500°C for 2 h

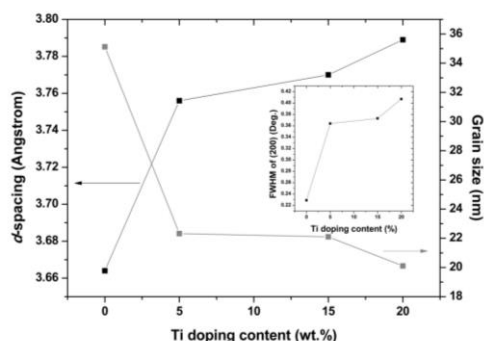


Figure 2. Interplanar spacing and grain size of Ti-doped WO₃ thin films prepared by the sol-gel spin coating method and annealed at 500°C for 2 h

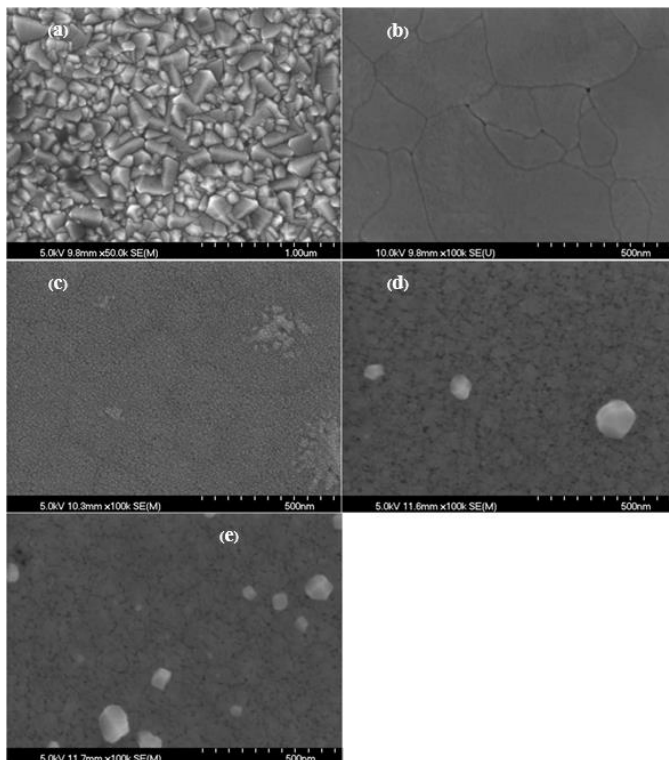


Figure 3. Surface morphology of Ti-doped WO_3 thin films annealed at 500°C for 2 h: (a) FTO, (b) undoped, (c) 5 wt% doped, (d) 10 wt% doped, and (e) 20 wt% doped

the sol-gel spin coating method. In addition, the grain size of the films can be reduced by doping with Ti ions.

The chemical bonding properties of the undoped and 20 wt% Ti-doped WO_3 film are shown in Figure 4. The noticeable bands located at about $3,450$ and $1,735\text{ cm}^{-1}$ correspond to the stretching and bending mode of the absorbed H_2O and O-H group by KBr molecules, respectively. The prominent vibration peaks of WO_3 are recognized at around 755 and 879 cm^{-1} relating to the stretching vibration of W-O-W and $\text{W}=\text{O}$, respectively (Aziz *et al.*, 2017). Meanwhile, the intensities of the characteristic vibration peaks decrease as the films were incorporated by the Ti dopant. It can also be noticed that the position of the W-O and $\text{W}=\text{O}$ stretching has slightly shifted toward a higher wavenumber in the 20 wt% Ti-doped WO_3 compared to the undoped WO_3

films. A blue shift is associated to the peak of the W-O and $\text{W}=\text{O}$ stretching owing to the alteration to a larger ionic size, lattice

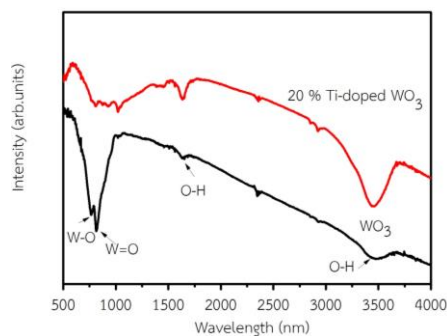


Figure 4. FTIR spectra of undoped and 20 wt% Ti-doped WO_3 thin films prepared by the sol-gel spin coating method and annealed at 500°C for 2 h

parameter, and bond length of the WO_3 lattice (Samanta *et al.*, 2018).

This result indicates that the appropriate doping of titanium ions into the WO_3 structure is well agreeable to the presumption from the XRD results.

The ultraviolet-visible (UV-Vis) transmittance spectra of pure and Ti-doped WO_3 with different Ti doping contents are demonstrated in Figure 5. From the results, the undoped WO_3 thin film shows the lowest optical transmittance in the visible and near infrared regions of about 70% and increases to 80% with Ti doping at 5 wt%. This result implies that the optical transmittance in the visible-near IR region can be improved by doping with Ti ions. The calculated optical band gaps of the films are illustrated in Figure 6, which are obtained from Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$, where α is the absorption coefficient, $h\nu$ is the photon energy, and the x-axis intercepted value is the optical band gap energy (Sarma and Sarma, 2018). Undoped- WO_3 and 5, 10, and 20 wt% doping give the optical band gap values of 3.29, 3.30, 3.38, and 3.39 eV, respectively. Furthermore, the blue shift of the absorption edge when the Ti dopants increase is observed that may be caused by the decreasing of the grain size of the WO_3 which can induce the increase in the optical energy gap of the films. These results are in harmony with the XRD and SEM results.

Figure 7 illustrates the optical transmittance in the bleached and colored states

of the Ti-doped WO_3 thin films. From the results, the undoped film shows the lowest transmittance in the colored and bleached states owing to the ions from the electrolyte still incorporated in the WO_3 film. On the other hand, in the bleached state, the 5 wt% Ti-doped WO_3 shows the highest optical transmittance. From the results, it is indicated that the ions from the electrolyte could be well ejected from the film in the bleached state.

The coloration efficiency (CE) of the films is computed from the optical density change (ΔOD), as in the following equation:

$$\Delta OD = \log(T_b/T_c) \quad (1)$$

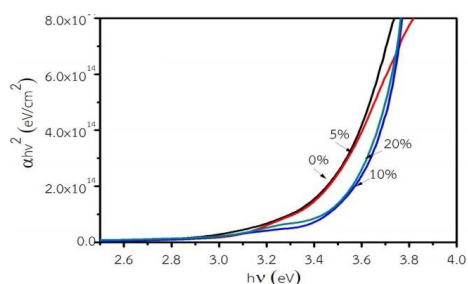


Figure 6. Tauc plots of Ti-doped WO_3 thin films prepared by the sol-gel spin coating method and annealed at 500°C for 2 h

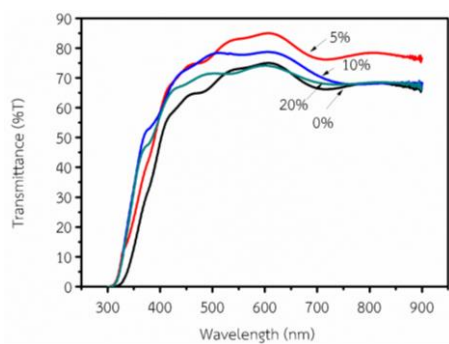


Figure 5. Transmittance spectra of Ti-doped WO_3 thin films prepared by the sol-gel spin coating method and annealed at 500°C for 2 h

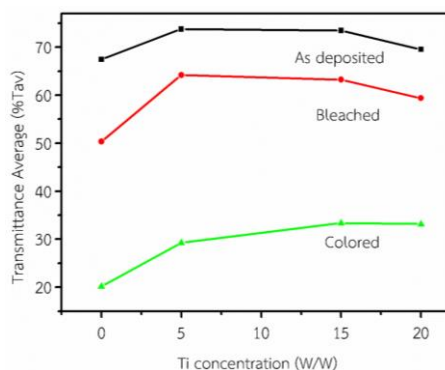
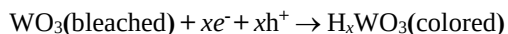


Figure 7. The average transmittance spectra in the bleached and colored states of Ti-doped WO_3 thin films with various Ti doping contents

where T_b and T_c are the bleaching and coloring transmittance state, respectively. Figure 8 demonstrates the optical density change in the wavelength 300-900 nm of the Ti-doped WO₃ thin films with various Ti doping contents. The results reveal that the 5 wt% Ti-doped WO₃ exhibits the highest optical density change in all the wavelength region owing to the deterioration of the WO₃ crystal by Ti doping. However, the optical density change decreases when the Ti doping content abundantly exceeds 5 wt% in consequence of the formation of amorphous TiWO₄ by heavy doping of Ti ions that can hinder the intercalation/de-intercalation of the ions (Yin *et al.*, 2018).

The CV of Ti-doped WO₃ thin films with various Ti doping contents is shown in Figure 9. From the results, the films with Ti doping at 0 wt%, 5 wt%, 10 wt%, and 20 wt% have the maximum peak positions at 0.05, 0.10, 0.10, 0.02, and -0.20 V corresponding to the anodic current of 0.518, 1.210, 0.757, and 0.838 mA, respectively. The CV plots reveal that the 5 wt% Ti-doped WO₃ shows the highest charges intercalation. The intercalation mechanism of the e^- and H^+ ions into the electrode produces the oxidation number of tungsten from W^{6+} to W^{5+} leading to the film getting a colored state owing to disorder of the WO₃ structure. The increase of the current from negative to a maximum value afterward decreases to zero corresponding to the coloration and bleaching of the films at varying voltages. During each

stage of this scan, the electrode undergoes a typical reversible color change from a colored to a bleached state. The recorded current is due to the ions intercalation/de-intercalation and the electron transport process according to the following electrochemical reaction:



From the electrochemical reaction, it reveals that the 5 wt% Ti-doped WO₃ demonstrates the highest anodic current peak owing to the deterioration of the WO₃ crystal by Ti doping. On the other hand, the decrease of the anodic peak current when increasing the Ti dopants over 5 wt% is mainly due to the formation of another amorphous phase, that is well agreeable to the presumption from the XRD, SEM, and ΔOD results.

Conclusions

In summary, Ti-doped WO₃ films were successfully deposited by the sol-gel spin coating process. The XRD results show the only monoclinic structure of WO₃ without a titanium-based impurity phase, suggesting the proper substitution of Ti ions incorporated into the WO₃ crystal structure resulting in a significant change of the d -spacing and grain size. The UV-Vis transmittance spectra exhibit the blue shift of the absorption edge of films

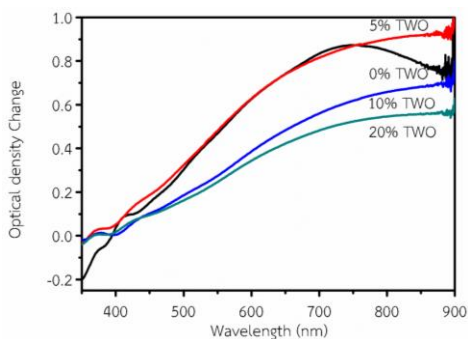


Figure 8. The optical density change in the wavelength 300-900 nm of Ti-doped WO₃ thin films with various Ti doping contents

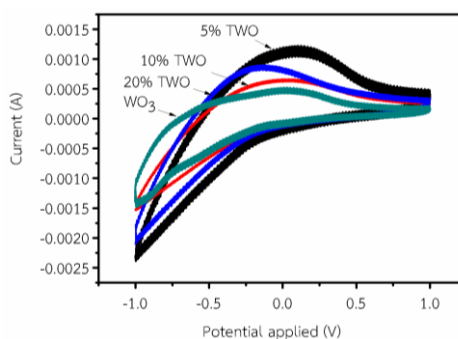


Figure 9. Cyclic voltammetry of Ti-doped WO₃ thin films with various Ti doping contents prepared by the sol-gel spin coating technique

that might be attributed to the grain size effect. The optical density change and CV plot indicate that the performance of WO₃ film applied as a smart window or energy storage can be enhanced by doping with Ti ions.

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