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# Influence of Ti and Zn Dopants on Structural Properties and Electrochromic Performance of Sol-Gel Derived $WO_3$ Thin Films

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**Abstract**

The influence of different transition metals doping (Ti and Zn) on structural properties and electrochromic adjustment and performance of sol-gel derived $WO_3$ thin films was conducted and investigated. Ti-doped $WO_3$ and Zn-doped $WO_3$ thin films were deposited onto F-doped tin oxide (FTO) substrates using spin coating technique. Tungsten powder, Titanium butoxide and zinc acetate dehydrate were used as starting precursors. The as-deposited films were annealed at 500 °C for 2 h. The effect of Ti and Zn doping on structural, surface morphologies, optical properties of the films were examined using X-ray diffractometer, scanning electron microscope and UV-VIS spectrophotometer. The XRD analyses suggest that the crystalline of $WO_3$ can be identified as a monoclinic $WO_3$ structure. XRD results additionally indicate the existence of $ZnWO_4$ structure in the Zn-doped films, which is clearly observed by SEM. The optical measurement of all films indicate good transparency in the visible region and near infrared region with more than 60% in transmittance. In addition, It was found that the electrochromic performance of $WO_3$ can be enhanced by small doping concentration of titanium due to structural modification of the films caused by close ionic radius of Ti to W rather than that of Zn.


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*Keywords* : Electrochromic, Zn doping, Ti doping, Tungsten oxide, Spin coating technique;

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## 1. Introduction

In the last decades, electrochromic phenomenon has been widely investigated owing to potential applications resulted from its reversibly changing color based on electrons insertion-extraction induced by external applied electric field. The transition metal oxide thin films are widely studied for electrochromic phenomenon. Among metal oxides, Tungsten trioxide ($WO_3$) is among feasible electrochromic materials that can be applied for practical utilization because of rather high optical reversible color change induced by electrochemical process that lead to their potential applications in smart windows, electrochromic windows, switchable devices and optical-based gas sensors [1]. $WO_3$ films have been fabricated by various techniques such as sputtering [2], chemical vapor deposition [3], pulsed spray pyrolysis [4], and sol-gel route [5]. Sol-gel based method is an attractive route used for the deposition of the films due to its simplicity, safety, ease of doping, high homogeneity, relatively low process temperature and facile control of the product chemical composition.

In previous published works, many efforts have been made to adjust structural and optical properties and functionality of practical electrochromic thin films by wide varieties of additives. Z. Wang *et.al* [6] prepared $TiO_2$-doped $WO_3$ thin films via the peroxo sol–gel and reported on the effect of annealing temperature on electrochromic properties of films. K. Paipitak *et.al* [7] showed that the influence of Ti doping on electrochromic performance of $WO_3$ films prepared by sol-gel method. R. Noonuruk *et.al* [8] successfully prepared $Zn_xNi_{1-x}O$ thin films by sol-gel method and reported on the effect of zinc content on ozone-induced coloration properties. X.F. Cheng *et.al* [9] gave a reported on the enhancement of photoelectrocatalytic performance of Zn-doped $WO_3$ thin films photocatalysts prepared by dip-coating for nitrite ions degradation under visible light. X. Chang *et.al* [10] synthesized transition metal-doped tungsten oxide nanostructures and explored the effect of different dopants on nanostructures

In this study, we report on the deposition of Ti-doped $WO_3$ (TWO) and Zn-doped $WO_3$ (ZWO) electrochromic thin films based on sol-gel spin coating technique and effect of Ti and Zn doping on structural properties, surface morphologies and electrochromic performance of the films were examined by mean of X-ray diffractometer (XRD), scanning electron microscope (SEM) and UV-Vis spectrophotometer.

## 2. Experimental

Ti-doped $WO_3$ (TWO) and Zn-doped $WO_3$ (ZWO) 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 carried out at 10-15°C which finally resulted to a pale yellow colored solution. After completely dissolved, ethanol solution and $Ti(Bu)_4$ (Aldrich) or $Zn(CH_3COO)_2{\cdot}H_2O$ (Aldrich) were subsequently added into the stock solution. The mixture was then stirred continuously for a few hours until the homogeneous starting precursor was obtained. Ti-doped WO3 and Zn-doped $WO_3$ thin films were deposited onto F-doped tin oxide (thickness~400 nm) conducting substrates with sheet resistance of 15 Ω/□. The sol-gel solution was coated by a spinner at speed of 2000 rpm. After each coating, the sample was post-baked at 100°C for 5 min and finally annealed at 500°C in ambient air for 2 hr. The influence of Ti and Zn doping on structural properties of the films were characterized by XRD. The surface morphology and film thickness were examined by SEM (Hitachi S-4700). The Optical properties of the films were investigated using UV-Vis spectrophotometer (Thermo Electron Corporation Heliosα).

## 3. Results and discussion

The X-ray diffraction patterns of undoped $WO_3$ and TWO thin films are illustrated in Fig. 1. It clearly shows well-defined crystallinity of $WO_3$ identified at $2\theta$ values of 23.1°, 24.3° and 28.6° assigning to monoclinic $WO_3$ (002), (200), (112) orientation planes, respectively [JCPDS 83-0950]. The existence of other diffraction peaks identified at 26.5°, 33.7°, 37.7° and 51.5° correspond to (110), (101), (200), (211) orientation plane of FTO substrate [11]. It is obviously noticed that the crystallinity of the $WO_3$ film drastically decreases with increasing of titanium content. When the films was doped with Zn as observed in Fig. 2, the crystallization of $WO_3$ slightly decreases as Zn doping concentration increases, accompanying the deterioration of the diffraction intensity of (200) orientation plane. In addition, it is noticeable that the appearance of obscure diffraction peak positioned at 30.5° due to mixed oxide of tungsten and zinc was formed $ZnWO_4$ in doped films [12]. Due to the fact that ionic radius of $Ti^{4+}$ of 0.62 Å that is slightly greater than that value of $W^{6+}$ (0.60 Å) but the ionic radius of $Zn^{2+}$(0.74 ˚A) is much larger than that of $W^{6+}$, it can be inferred that titanium ion and zinc ion may be incorporated into the $WO_3$ lattice by displacing some $W^{6+}$ ions without changing its monoclinic structure. In addition, the formation of other phase of monoclinic $ZnWO_4$ structure in Zn-doped films is existed due to the difficulty of substitution of Zn into $WO_3$ latticed resulted from quite ionic radius difference between them. This feature is in good agreement with previous literature conducted by X.F. Cheng *et.al.* [9].

Fig. 3(a) and (b) exhibit the cross-section image of TWO and ZWO thin films deposited on FTO substrates. It can be observed that the average thickness evaluated from SEM image is approximately 158 nm and 250 nm, respectively. The surface SEM micrographs of undoped, TWO and ZWO thin films are illustrated in Fig. 4(a) - (c), respectively. Morphology of undoped film is displayed in Fig. 4a. Film surface possesses distinct large grains. When doping with titanium and zinc, the grains of $WO_3$ exhibit significant decrease in their size with titanium and zinc doping. On the other hand, ZWO images indicate that morphologies of films comprise well crystallization of oxide compounds of Zn and W. The SEM results are agreeable to XRD results and in good accordance with previous work reported by A.R. Phani *et.al.* [12] who synthesized $ZnWO_4$ by conventional solid state method. The formation of $ZnWO_4$ film by this deposition technique was also confirmed by EDX results (Fig. 5), which indicated the presence of tungsten and zinc element in these patterns as listed in table 1.

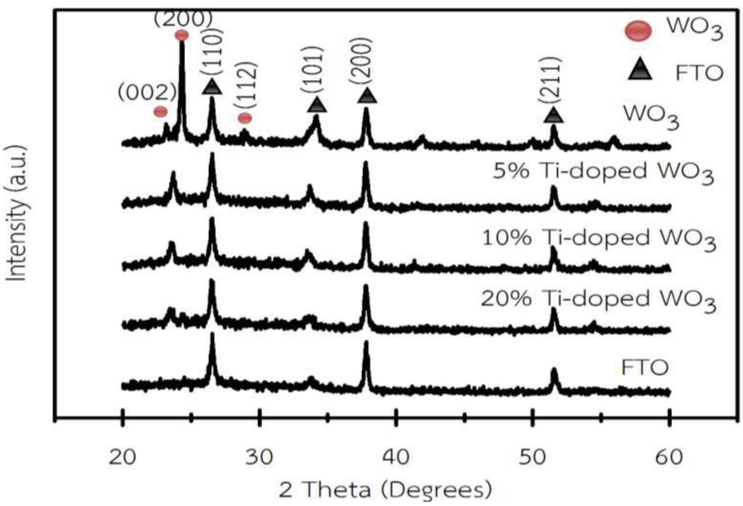


Fig. 1. XRD patterns of undoped $WO_3$ and TWO thin films with different Ti doping concentration of 5 wt%, 15 wt%, and 20 wt%.

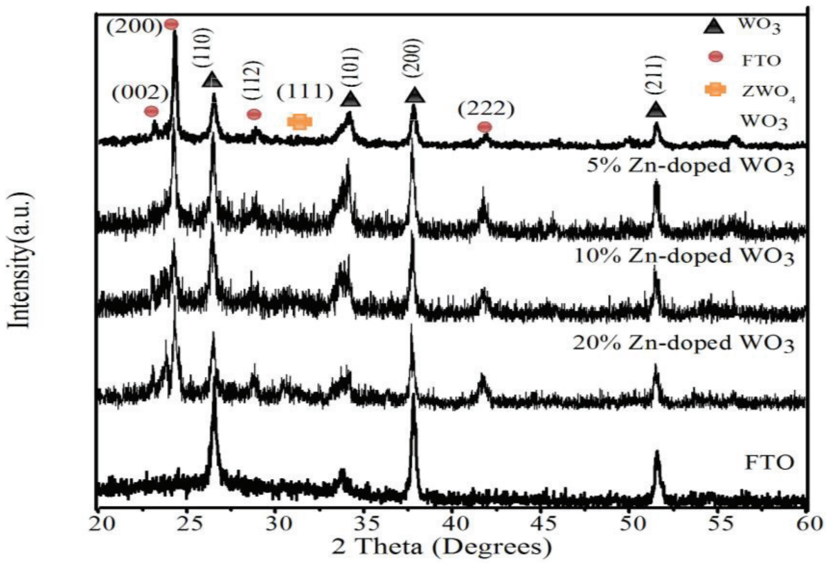


Fig. 2. XRD patterns of undoped $WO_3$ and ZWO thin films with different Zn doping concentration of 5 wt%, 15 wt%, and 20 wt%.

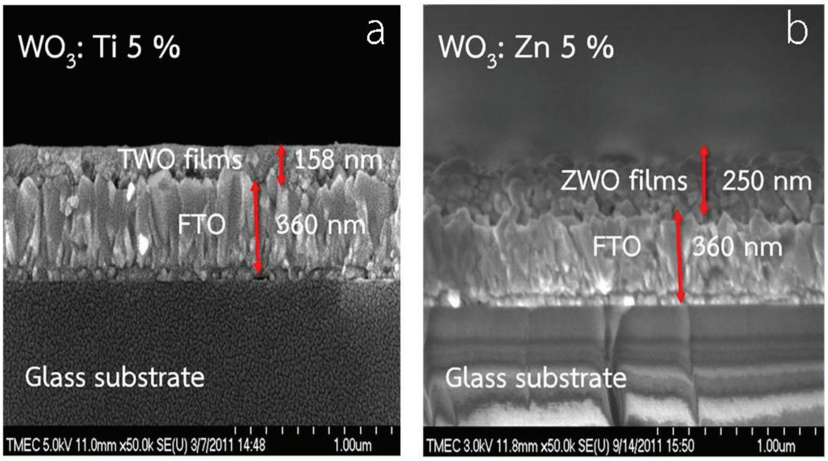


Fig. 3. Cross-section images of TWO and ZWO thin films.

The electrochromic measurements were carried out in 0.001 M of $H_2SO_4$ electrolyte. The corresponding transmittance spectra of undoped film, TWO and ZWO films in the as-deposited, colored ($T_c$) and bleached state ($T_b$) is shown in Fig 6(a)-(c). The results show that as-prepared films are highly transparent with corresponding transmittance of 70% in the visible and near infrared region.

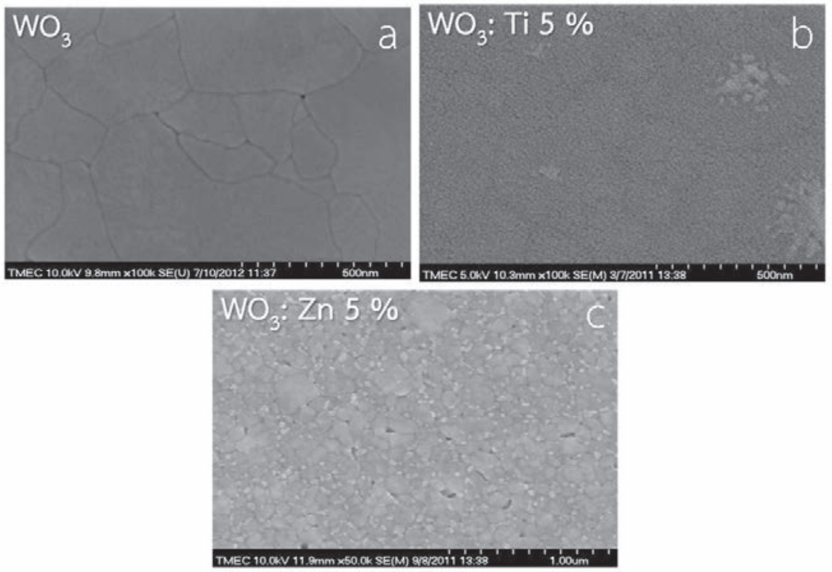


Fig. 4. Surface morphology images of undoped $WO_3$, TWO and ZWO thin films.

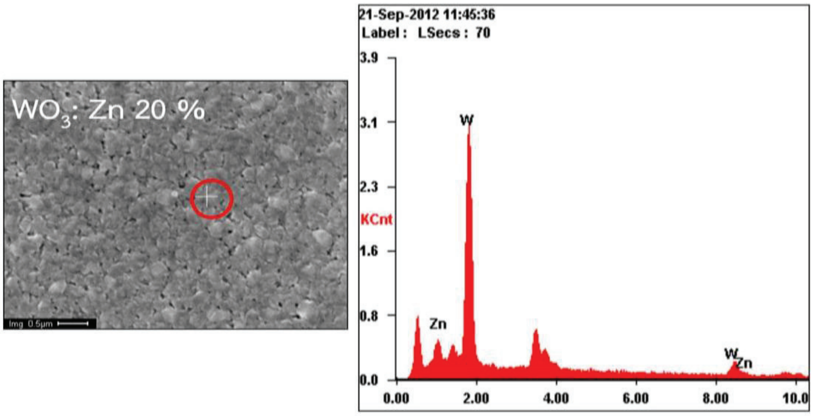


Fig. 5. EDX spectra of Zn-doped $WO_3$ thin film.

Table 1. The elements of ZWO thin film.

| Element | Wt% | At% |
|---|---|---|
| W | 90.87 | 77.96 |
| Zn | 9.13 | 22.04 |

The color of the film changes to deep blue color when $H^+$ ions and electrons are inserted into these films. It is clearly indicated that the TWO film with 5% doping content has a good colored state and the transmittance in a bleached state was apparently higher than undoped and ZWO film, implying the superiority in electrochromic performance of this film. The transmission change (ΔT) values of all films measured at wavelength region of 600-650 nm is concluded in table 2. The results exhibited that the TWO film with 5% doping content has superiority in transmission change, comparing the others. The percent transmittance at bleached state was approximately 65.19%, while the colored state was about 29.23% corresponding to a transmittance change value of ΔT= 34.96. It is noticed that the enhancement of electrochromic performance and reversibility of $WO_3$ can be attained by certain amount of Ti additive. On the other hand, the transmittance change of Zn doping decreases reflecting that inferiority of electrochromic performance due to large difference between ionic radius of $Zn^{2+}$ and that of $W^{6+}$ that can lead to the formation of other phase of $ZnWO_4$ structure in doped films.

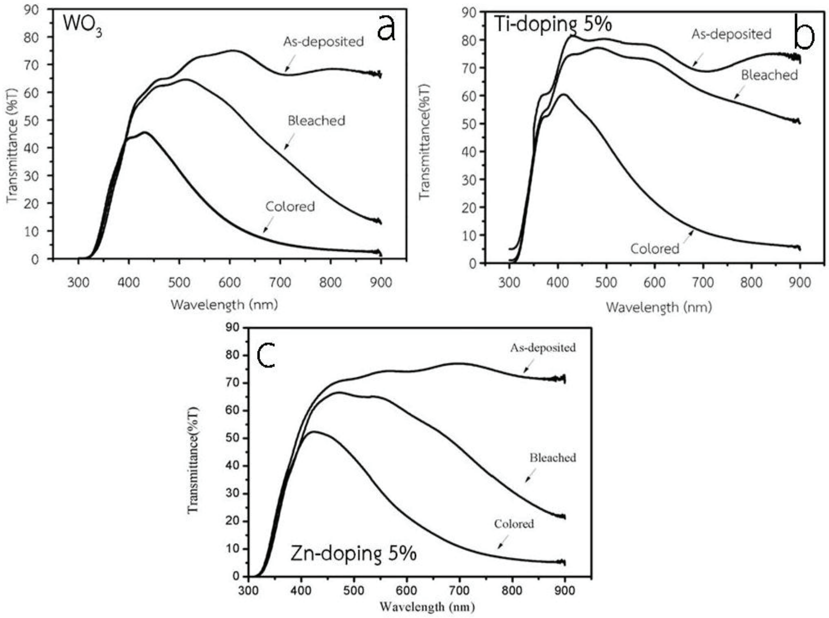


Fig. 6. Transmission spectra of colored and bleached state of (a) undoped film, (b) TWO film with 5% Ti doping content and (c) ZWO thin films with 5% Zn doping content.

Table 2. The transmittance measurement of undoped, ZWO and ZWO thin films.

| Type of films | Transmittance at bleached state $T_b$, (%) | Transmittance at colored state $T_c$, (%) | Transmission change (ΔT) = ($T_b$-$T_c$) |
|---|---|---|---|
| $WO_3$ | 50.33 | 20.13 | 30.20 |
| TWO | 65.19 | 29.23 | 34.96 |
| ZWO | 55.70 | 27.77 | 27.93 |

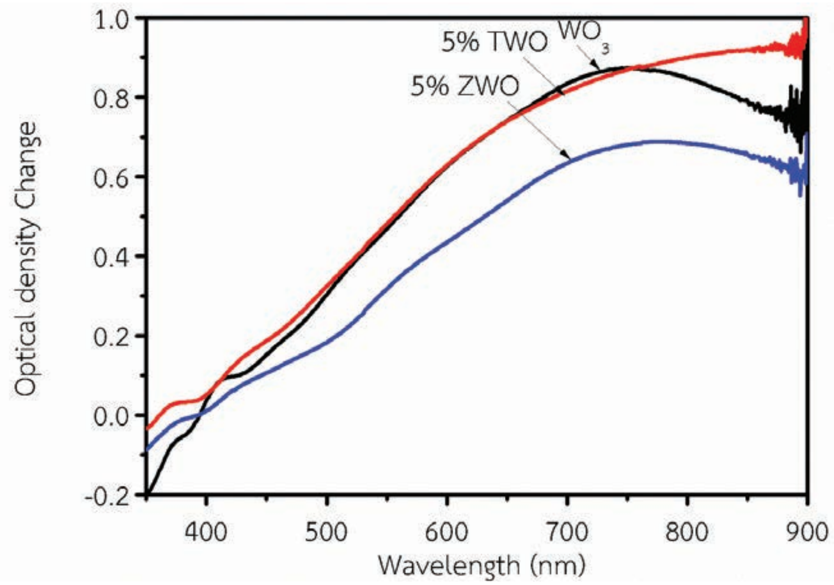


Fig. 7. Optical density change of undoped, ZWO and ZWO thin films.

The coloration efficiency of electrochromic film can be also defined as the change in the optical density (ΔOD) calculated from Eq. (1)

$$\Delta OD = \log \frac{T_b}{T_c} \qquad (1)$$

where $T_b$ is the bleaching transmittance and $T_c$ is the coloring transmittance. Fig. 6 shows the optical density change (ΔOD) of undoped, TWO and ZWO films. It can be seen that, the ΔOD increases with Ti doping but decreases with Zn doping. The results indicated that TWO has significant improvement in coloration efficiency of the film. This result suggests that the enhancement of coloration efficiency of the film by the accompaniment of Ti doping.

## 4. Conclusion

In conclusion, Ti-doped $WO_3$ and Zn-doped $WO_3$ thin films were successfully prepared by sol-gel spin coating technique. The XRD results reveal that as-prepared films possess monoclinic $WO_3$ structure. Ti and Zn additive doped into $WO_3$ thin film leads to the deterioration of the film crystallinity and effect of Zn doping revealed the occurrence of $ZnWO_4$ structure in doped films. SEM results validate the decrease in grain size of $WO_3$ with titanium and zinc doping. The EDX measurement was conducted and corresponding results confirm the existence of doping element in the doped films. The coloration efficiency was measured and the corresponding results disclose that Ti doping could lead to significant improvement in coloration efficiency of the film due to closer ionic radius to W, comparing to Zn.

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