

XPS Study in Electrochromic Process of Zn-doped NiO and Zn-doped WO₃ Thin Films Prepared by Spin Coating Method

Orawan Thanomkiat^{1*}, Kanokkorn Paipitak², Russameeruk Noonuruk², and Wanichaya Mekprasart²

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

²College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang Ladkrabang, Bangkok, 10520 Thailand

Abstract

Variation in oxidation states of Ni, W and O in electrochromic process of Zn-doped NiO and Zn-doped WO₃ sol-gel derived thin films deposited by spin coating technique were extensively investigated by mean of X-ray photoelectron spectroscopy. The starting precursors for NiO and WO₃ thin film deposition were prepared from nickel acetate tetrahydrate and tungsten powder dissolved in hydrogen peroxide meanwhile Zn dopant was started from zinc acetate dehydrate. X-ray photoelectron spectroscopy measurement was conducted on colored and bleached states of electrochromic process of both films. The corresponding results exhibited the significant variations of oxidation states and compositions of Ni ion, W ion and O were observed and were in good agreement with proposed chemical reactions during electrochromic process. The role of Zn dopant on electrochromic performance of both NiO and WO₃ films was also investigated

Keywords: NiO, WO₃, Electrochromic, X-ray photoelectron spectroscopy

1. Introduction

Electrochromism is recently a key technology for efficient energy conservation. Up to now, tungsten oxide (WO₃) and nickel oxide (NiO) are of the most extensively used materials for practical applications such as smart windows, mirrors, electrochromic windows, switchable devices and sensors [1]. In particular, both tungsten oxide and nickel oxide has been widely applied as a key active electrochromic material for smart windows, which possess variable light transmission characteristics and may be useful for applications in buildings or car industries. Several of deposition techniques are available for thin film coatings including sputtering [1, 2], chemical vapor deposition [3], electron beam deposition [4], pulsed spray pyrolysis [5], and sol-gel spin coating [6]. The sol-gel method generally gains significant advantages such as controllable chemical composition, cost-effectiveness of equipment and precursors, good homogeneity, low operating temperature and ease of doping. More recently, a number of attempts have been taken in order to enhance the electrochromic performance by the incorporation of metal doping such as Ti, V, Co, Fe, and Zn [7]. Nevertheless, based on our recent knowledge, original works focusing on the preparation and electrochromic investigation of WO₃ and NiO thin films doped with Zn element that is available in the reports are still scanty. In this work, spin coating was utilized for depositing Zn-doped NiO and Zn-doped WO₃ optical thin films onto FTO substrates in combination with heat treatment. The effect of Zn additive on physical and electrochromic properties of the films were investigated by X-ray photoelectron spectroscopy (XPS) measurement was conducted. Typically, XPS is an important technique for analyzing the

chemical states and elemental compositions of the films. Because the electrochromic phenomenon generally relates to the change in oxidation state of materials and the appropriate composition of Zn additive is significant to enhance the electrochromic properties, XPS is therefore a suitable characterization technique to probe the change of oxidation state during the chromic process.

2. Experimental Details

Zn-doped WO₃ (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 performed at 10-15°C which finally resulted to a pale yellow solution. After completely dissolved, ethanol solution and certain doping amount of Zn(CH₃COO)₂·H₂O (Aldrich) were subsequently added into the stock solution. The mixture was then stirred continuously until homogeneous starting precursor was obtained. Zn-doped WO₃ electrochromic 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 baked at 100°C for 5 min and was finally annealed at 500°C in ambient air for 2 h.

Meanwhile, Zn-doped NiO (ZNO) thin films were deposited onto F-doped tin oxide (FTO) (15Ω/□) substrates by the sol-gel spin-coating technique. The sol-gel precursor was prepared by mixing of 0.3 M nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) and zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) dissolved in 50 ml absolute ethanol and 2.5 ml-diethanolamine (HN(CH₂CH₂OH)₂, DEA) performed as sol-stabilizing agent was added into the precursor. The concentration of Zn additive was controlled at 0% (undoped), 5%, 10% and 20%. The mixed solution was kept under vigorous stirring at 70°C for 2 h and then was aged for 24 h at room temperature. The sol-gel precursor was coated on FTO substrates by spinner at speed of 2500 rpm for 50 sec. After the spin coating, the films were dried at 100°C for 10 min to evaporate the solvent and the coating was repeated for 10 times. Finally, the deposited films were annealed in furnace at 350°C for 2 h to remove organic residuals. The surface chemical state analysis was investigated by XPS (Kratos analytical, AXIS ULTRADLD) using AlKα with radiation at 1.4 keV. The optical density change, which is optical difference between colored and bleach state, was characterized by UV-Vis spectrophotometer (PG Instruments, T90).

3. Results and Discussion

The chemical composition characterization and valance states of ZWO thin film was investigated using X-ray photoelectron spectroscopy (XPS). Fig. 1 shows the XPS survey scan spectra of the film in the binding energy range of 0–1200 eV. It can be seen that the characteristic peak of tungsten, zinc, oxygen with carbon as a reference peak are prominent and distinct affirming the existence of relevant elements in the deposited films.

Fig.2 (a) shows detailed spectra of W4f core level spectra for as-deposited on ZWO film. The results exhibited spin-orbit-splitting doublet peak corresponding to W4f_{7/2} and W4f_{5/2} with the binding energy of 35.48 and 37.58 eV, respectively, indicating the majority of the oxidation state of the W⁶⁺ state. It clearly shows that the as-deposited ZWO film contains only the W⁶⁺ state. The XPS spectra of W4f for ZWO film in the colored state are shown in Fig.2 (b). The major peak positions of the first doublet observed at the binding energy of 35.48 and 37.58 eV, correspond to W⁶⁺ f_{7/2} and 4f_{5/2}, respectively. The second peaks at the

binding energies of 36.28 and 38.51 eV are ascribed to $W^{5+} 4f_{7/2}$ and $4f_{5/2}$, that are in contrast to the as-deposited film. The third peaks are at the binding energies of 33.5 and 35.1 eV,

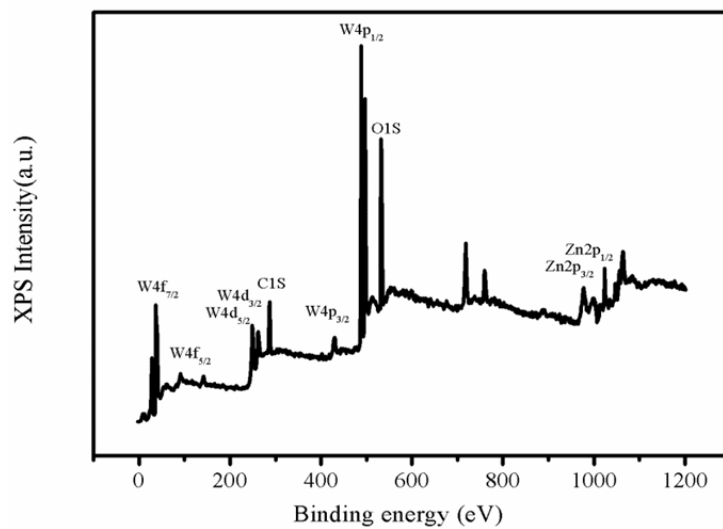


Fig. 1. The XPS survey scan spectra of Zn-doped WO_3 thin film.

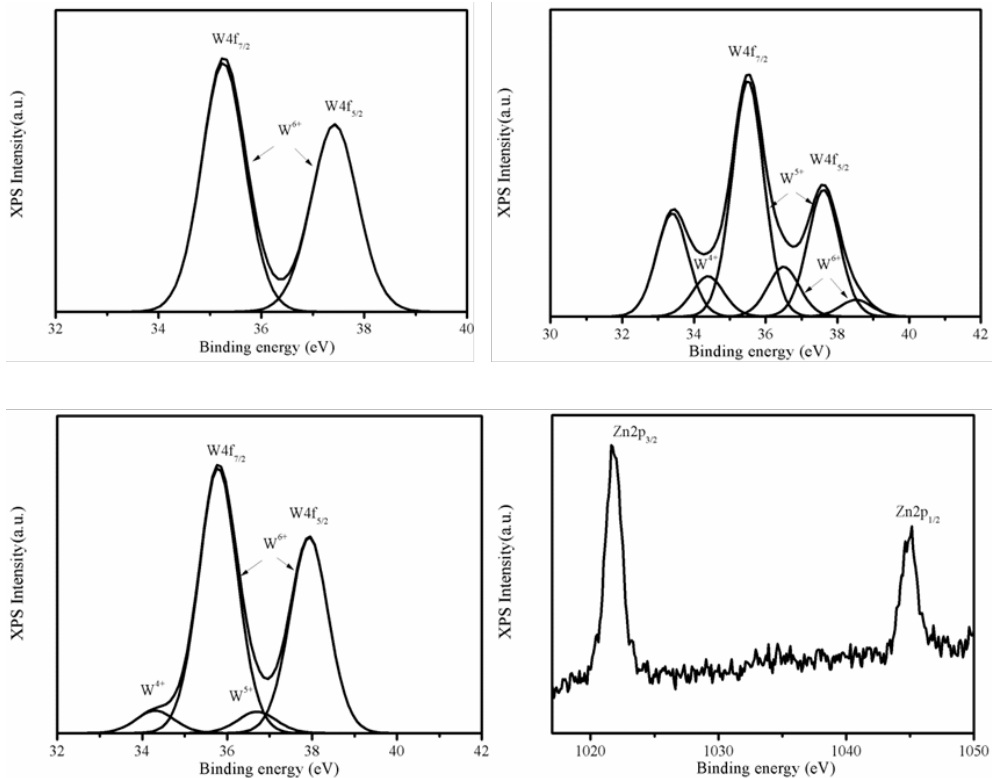
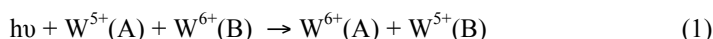


Fig. 2. The XPS spectra of W4f for ZWO film.

corresponding to $W^{4+} f_{7/2}$ and $4f_{5/2}$, respectively. The results exhibited that the proportion of W^{6+} ion are reduced to W^{4+} and W^{5+} ion at color stage due to the small polaron transition between W^{5+} and W^{4+} ion instead of W^{5+} and W^{6+} ion by injection of ion and electron in the film during the coloration process. Schirmer's [8] proposed that the optical absorption is caused by small polaron when electrons polarize their surrounding at tungsten lattice so changing the valence of the tungsten ions from W^{6+} to W^{5+} . Incident photons are hence absorbed by small polarons with hopping between neighboring W sites. This process which is typically extracted from the following expression;



The XPS spectra of W4f for ZWO film in the bleach state are shown in Fig.2 (c). The major peak positions of the first doublet peak are at 35.91 and 38.05 eV, corresponding to the W^{6+} , and the other doublet are positioned at 32.9 and 35.1 eV and is ascribed to the W^{4+} . The decrease in the W^{5+} in the film indicated the ion and electron extraction during the bleaching process. The XPS for Zn2p core level spectra is illustrated Fig. 2(d). The doublet spectra of Zn2p core level peaks are observed at binding energy of 1022.0 and 1045.3 eV, which are assigned to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively [9].

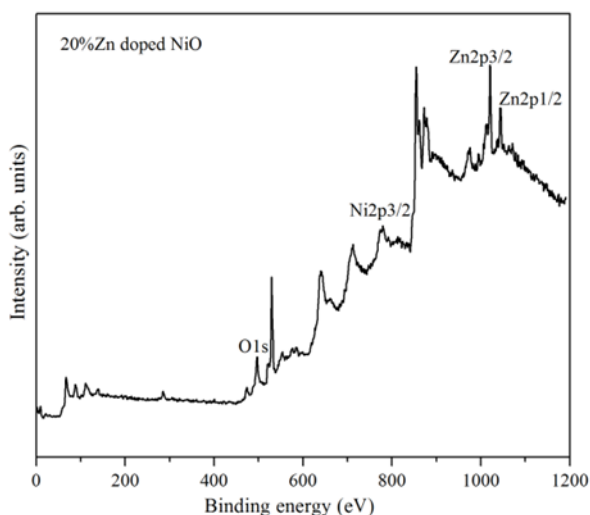


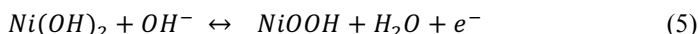
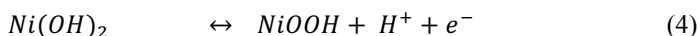
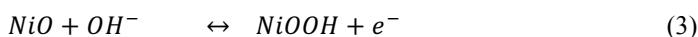
Fig. 3. The XPS survey scan spectra of Zn-doped NiO thin film.

The XPS survey spectrum of Zn-doped NiO film is illustrated in Fig. 3, indicating the appearance of O, Ni and Zn with corresponding binding energy of 529.4 eV, 854.4 eV and 1020.4 eV, respectively. This result confirms the existence of implicated elements of prepared film. As seen in Fig. 4(a) and (b), Ni 2p spectra detected in two regions of 850-865 eV and 870-875 eV correspond to the spin orbital state of 2p_{3/2} and 2p_{1/2}, respectively. Ni 2p_{3/2} state of undoped film exhibits the double peaks characteristic correlating to NiO and Ni(OH)₂ at binding energy of 853.6 and 855.2 eV, respectively [10]. For doped film, the double peaks structure of Ni 2p_{3/2} state obviously tends to merge into approachable single peak. In general, the lower binding energy at 853.6 eV is a typical main state of Ni 2p_{3/2} and the higher binding energy at 855.2 eV is ligand hole transformation from core ionized site to the next-neighbor cluster [11]. With an incorporation of Zn into NiO films, the chemical

strength between Ni and O is weakened, accompanying the noticeable decrease in intensity the lower binding energy of 853.6 eV. This feature additionally notifies the optimized condition of Zn composition in NiO film for the enhancement of coloration performance. In bleaching process, color of the films could rapidly change from deep brown color to be almost transparent like as-prepared condition, indicating the good electrochromic feature of these films prepared by sol-gel method. Alternatively, the coloration of the film can be evaluated by corresponding optical density change (ΔOD) expressed as;

$$\Delta OD = \log \frac{T_b}{T_c}, \quad (2)$$

where T_b and T_c are the transmittance of bleached state and colored state, respectively. The ΔOD values of NiO and Zn-doped NiO films at wavelength of 550 nm are illustrated in Fig. 5. The ΔOD value of the film increases with increasing Zn-doping content. The ΔOD value indicates that the film with 10% Zn doping composition performs superiority in electrochromic efficiency to the others. This feature may be attributable to the fact that Zn additive incorporated into NiO film can significantly reduce the crystallinity and grain size of NiO, resulting in greater active surface area for the ease of charge extraction/insertion into the film. The general model for the coloring and bleaching process is reversible transformation between NiOOH and Ni(OH)₂ phases or Ni³⁺/Ni²⁺ in redox process [12]. H. Kamal and co-workers reported the several electrochemical reactions depending on coating techniques after cumulated the reaction mechanism in different preparations of NiO thin films [13]. The commonly accepted electrochemical reactions in the aqueous electrolytes are as follows:



Bleached

Colored

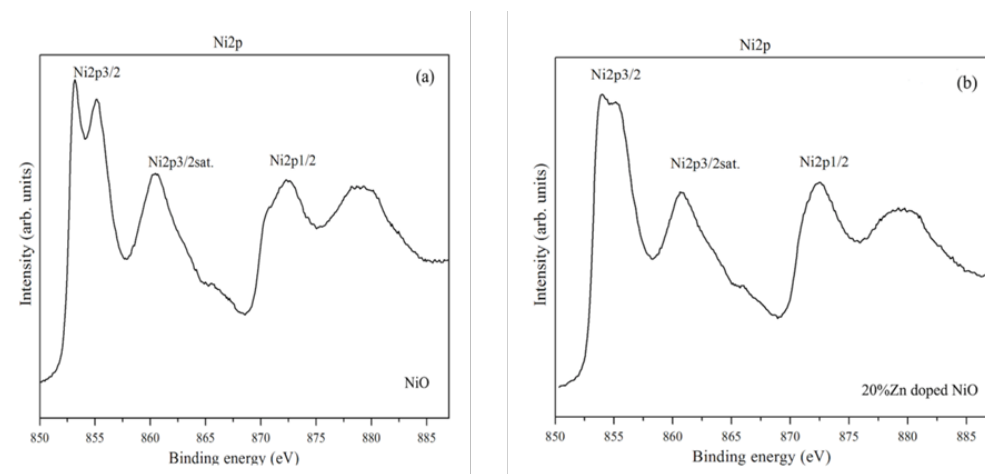


Fig. 4. Ni 2p XPS spectra of the (a) NiO film and (b) 20%Zn-doped NiO film.

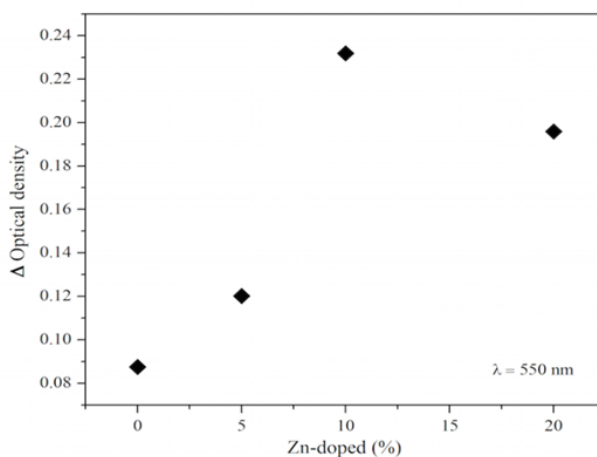


Fig. 5. Optical density change of NiO thin film with different Zn doping content measured at $\lambda = 550$ nm.

The electrochromic mechanism of Zn-doped NiO thin films can be interpreted from XPS spectrum of O1s state in oxide phase. The O1s states of 20%Zn-doped NiO thin films in as-deposited, colored and bleached state are shown in Fig.8(a), (b) and (c), respectively. The O1s spectra of all states exhibit two noticeable peaks with binding energy of 529.10 and 531.02 eV, which relate to oxygen in the NiO lattice and the surface adsorption of H_2O or OH^- , respectively [14]. In the initial electrochemical process, the $Ni(OH)_2$ phase is formed chemically on the surface of NiO by immersion in KOH solution according to following equation [15]:



In coloring process, the amount of adsorption of OH^- increases accompanying the increasing intensity of the spectrum at 531.02 eV meanwhile the intensity of spectrum due to oxygen in the lattice is consistent with as-deposited state. The intercalation of OH^- ions into the film leads to the formation of $NiOOH$ species according to equation (5). In bleaching process, the intensity of this spectrum decreases slightly, implying to the possible transformation from $NiOOH$ to $Ni(OH)_2$ due to OH^- extraction from the film. These results suggest that the electrochromic mechanism of this sol-gel derived NiO film is caused by the insertion/extraction of OH^- that can be described by corresponding process expressed in equation (5).

4. Conclusion

The Zn-doped WO_3 and Zn-doped NiO thin films were prepared by sol-gel method. X-ray photoelectron spectroscopy was conducted on these thin films in order to investigate the alternation in oxidation state of relevant elements during electrochromic process. In ZWO thin films, the XPS results suggest that the electrochromic mechanism of this film is mainly associated with the alternation of W^{6+} , W^{5+} and W^{4+} . Meanwhile the electrochromic activity of ZNO is generated by the insertion/extraction of hydroxyl group that is supported by XPS results. These occurrences imply that amorphous phase of NiO films favors the efficient

contact between active materials and electrolytes, providing more active sites for electrochemical reactions and resulting in higher color contrast.

Acknowledgements

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