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Electrochromic Nb-doped WO_3 films: Effects of post annealing

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Abstract

The Nb-doped WO_3 films were deposited by e-beam co-evaporation method using ceramic WO_3 targets and metal Nb slugs. The films were analyzed by glancing incident angle X-ray diffraction (GIAXRD), UV/visible spectrophotometer, electrochemical cyclic voltammetry, X-ray photoelectron spectroscopy (XPS). The as-prepared film is brown and amorphous in structure. The film has low transmission in optical visible region. The XPS results indicate that the as-deposited film is non-stoichiometric. By applying a negative potential, the as-deposited film does not show obvious electrochromic effect. However, the electrochromic properties of Nb-doped WO_3 films are improved by post annealing treatment at 350, 400, and 450 °C in oxygen atmosphere. The Nb-doped WO_3 films transform into crystalline structure and become transparent after post annealing treatment. The energy band gap, optical modulation, and color efficiency increase with annealing temperature.

Keywords: Electrochromism; WO_3; Annealing; E-beam evaporation

1. Introduction

The electrochromic materials possess the ability of reversible and persistent change of optical properties by double insertion/extraction of electrons and counter ions (H^+, Li^+.) [1,2]. This unique property makes electrochromic materials of great interest for application in different types of optical devices, such as display, rear view mirror, and smart windows [3–6]. Among diverse electrochromic materials, tungsten oxide (WO_3), which turns blue upon electrochemical insertion and becomes transparent upon extraction, is by far the most extensively studied materials prepared by vacuum evaporation [7–9], chemical vapor deposition [10], hydrothermal [11] sol–gel [12,13], sputtering [14,15] and electrodeposition [16]. For a few years, there is an extensive study for the improvement of the properties of tungsten oxide by addition of enhanced dopant [17–23]. Some compounds, such as TiO_2, MoO_3 and Nb_2O_5, are used to increase coloration efficiency, cycling lifetime, or reaction kinetics. Bathe and Patil [21] shows that the cycle stability, charge storage capacity, and reversibility can be improved by addition of Nb_2O_5 into WO_3 films. Avellaneda's study [24] indicates the mixed Nb_2O_5–WO_3 films have larger optical modulation in photochromic reaction. Rougier et al. [19] showed that the W–Nb–O films possess the property of color neutrality which is promising for building application in reduced state. However, there are few studies on the effect of post annealing on electrochromic Nb-doped WO_3 films. In this study, we prepared Nb-doped WO_3 films by electron evaporation method and investigated the influence of post annealing treatment on the electrochromic properties.

2. Experimental procedure

The Nb-doped WO_3 films are prepared by electron beam co-evaporation method. The deposition targets are ceramic WO_3

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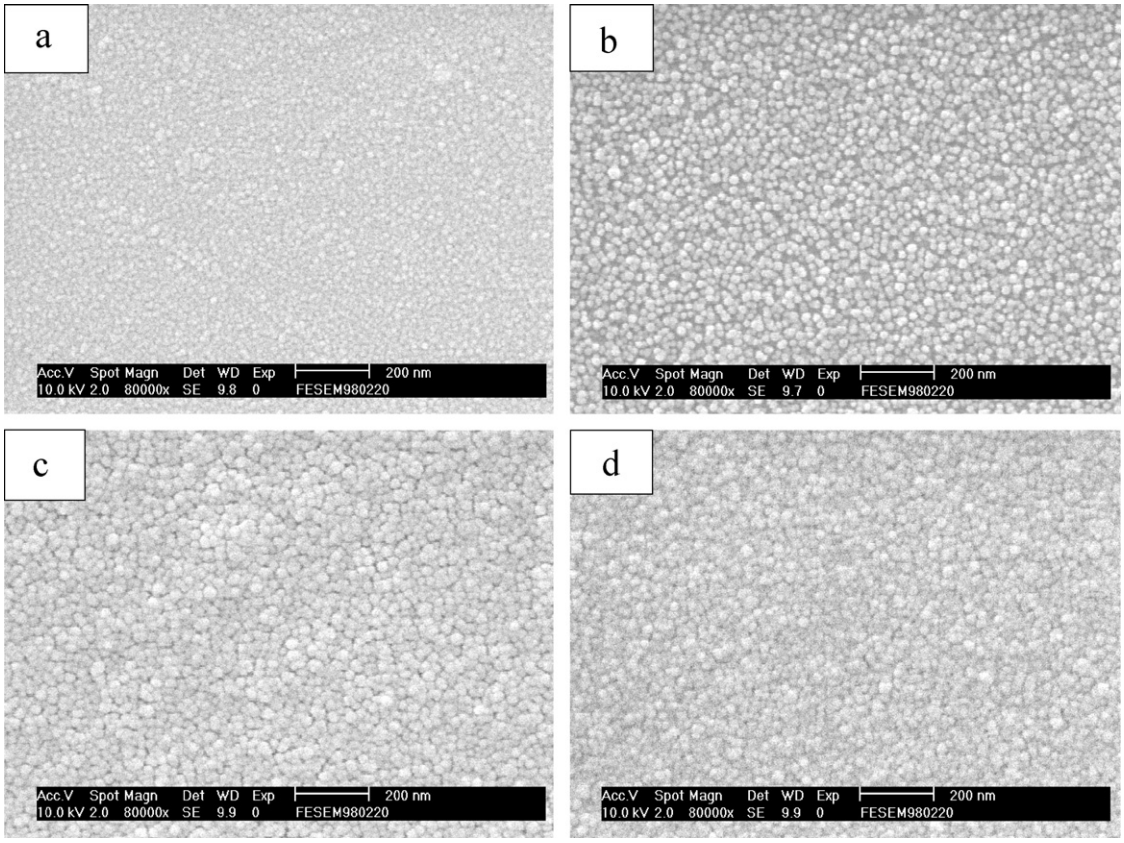

Fig. 1. SEM images of (a) as-deposited and heat-treated films at (b) 350, (c) 400, (d) 450 °C in O_2 atmosphere.

bulks and metal Nb slugs. Before deposition, the vacuum chamber is evacuated to 1.07×10^{-4} Pa and the deposition pressure is controlled at 6.67×10^{-5}–2.67×10^{-4} Pa. After deposition, the Nb-doped WO_3 films are post annealed in O_2 atmosphere at 350, 400, and 450 °C for 2 h.

The film crystal structure was examined by Rigaku DMAX 2500 diffractometer with Cu K_α radiation of wavelength 0.1542 nm. The film surface morphology was studied by Philips XL40 field emission scanning electron microscopy (FE-SEM). The optical transmittance spectrum was measured by Hitachi U-2001 UV/Visible Spectrophotometer in the range of 300–1100 nm. The composition distribution profile and surface chemical state were inspected by X-ray photoemission spectroscopy (PHI 5000 VersaProbe). The X-ray excitation source is Al K_α radiation of energy 1486.6 eV. The carbon 1s peak with binding energy 284.6 eV is used to calibrate tungsten and niobium binding energy. The cycling voltammogram tests were carried out on VersaStat II Electrochemical Workstation with three electrodes configuration. The counter and reference electrodes were platinum and saturated calomel electrode (SCE). The electrolyte was 0.1 M LiClO4/propylene carbonate (PC) solution.

3. Results and discussion

The thickness of the Nb-doped WO_3 films deposited by electron beam co-evaporation is about 350 nm. The as-deposited film contains 27.79% W, 17.30% Nb, and 53.1% O and the composition is well distribution, as examined by XPS. Fig. 1 shows the morphology of Nb-doped WO_3 films for as-deposited state and the post annealed films at 350, 400, 450 °C in O_2 atmosphere. It is observed that grain size increases with annealing temperature.

Fig. 2 shows the GIAXRD patterns of Nb-doped WO_3 films at three different postannealing temperatures in O_2 atmosphere. The GIAXRD pattern of as-prepared film is amorphous structure without any obvious diffraction peaks. After post annealing process, a diffraction peak at 25° appears and the peak intensity increases with post annealing temperature. It can be explained by the fact that the electrochromic films have crystallized by post annealing treatment. Compared to the Bathe's results [21], the GIAXRD patterns do not reveal the formation of solid solution WNb_2O_8 even after annealing at 450 °C in O_2 atmosphere. This difference may be caused due to different preparation methods. Bathe prepared W–Nb–O films by sol–gel method in which the chemical activity of precursor is higher than that of atomic evaporation method. The as-deposited Nb-doped WO_3 film is deep brown color and the optical transmittance is below 20%. The optical transmittance of Nb-doping WO_3 film is increased by post annealing process in O_2 atmosphere, as shown in Fig. 3. The optical transmittance of Nb-doped WO_3 increase gradually from as-deposited state to 400 °C post-annealed film and the optical transmittance of Nb-doping WO_3 film does not increase further even after post annealing at 450 °C. The film color becomes transparent after

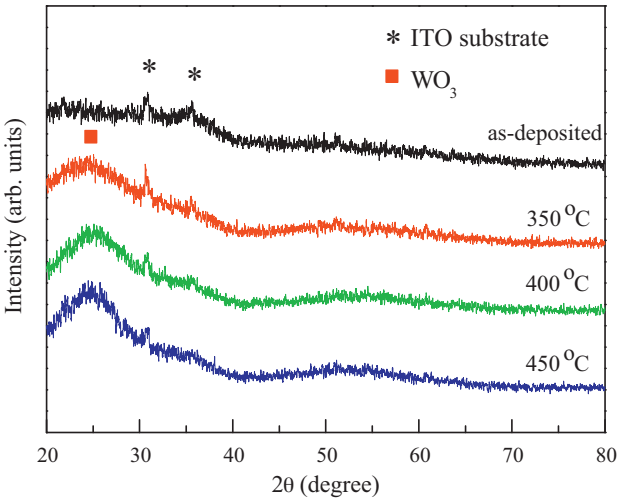

Fig. 2. The GIAXRD patterns of Nb-doping WO_3 film after three different postannealing temperatures in O_2 atmosphere.

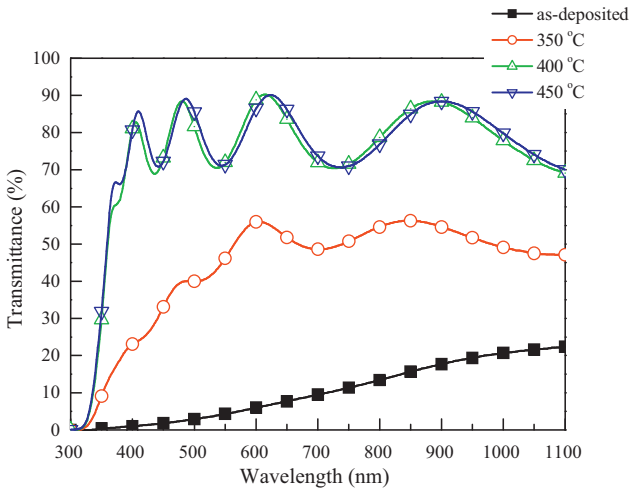

Fig. 3. The optical transmittance spectra of Nb-doped WO_3 films at as-deposited state and after post annealing treatment at 350, 400, and 450 °C in O_2 atmosphere.

heat treatment at 400 and 450 °C in O_2 atmosphere. The band gap energy can be calculated from Tauc's law [25] using the relation of $(\alpha hv)n = A(hv - E_g)$, where α is the absorption coefficient, n is a characteristic constant depends on the material, A is a constant, and E_g is the band gap energy of the film. For the indirect allowed transition Nb-doped WO3 films, n is equal to 2. The band gap energy of Nb-doped WO_3 films are 1.98, 3.58, 3.69, and 3.69 eV for as-deposited state and annealed films of 350, 400, and 450 °C, respectively. The variation of band gap energy could be caused by the increase of chemical stoichiometry and crystal growth effect. The chemical states of W and Nb atoms of as-deposited and annealed film at 450 °C are examined by XPS and the results shown in Fig. 4. The W4f XPS spectra contain three major peaks at 33.2, 35.4 and 37.6 eV. Those peaks can be decomposed into two doublets of W^{+6} (35.6, 37.7 eV) and W^{+4} (32.9, 35.1 eV) ions of W 4f7/2 and W4f5/2 [26]. The XPS spectra of Nb atom for as-deposited state show two major peaks at 207.2 and 209.8 eV and a small

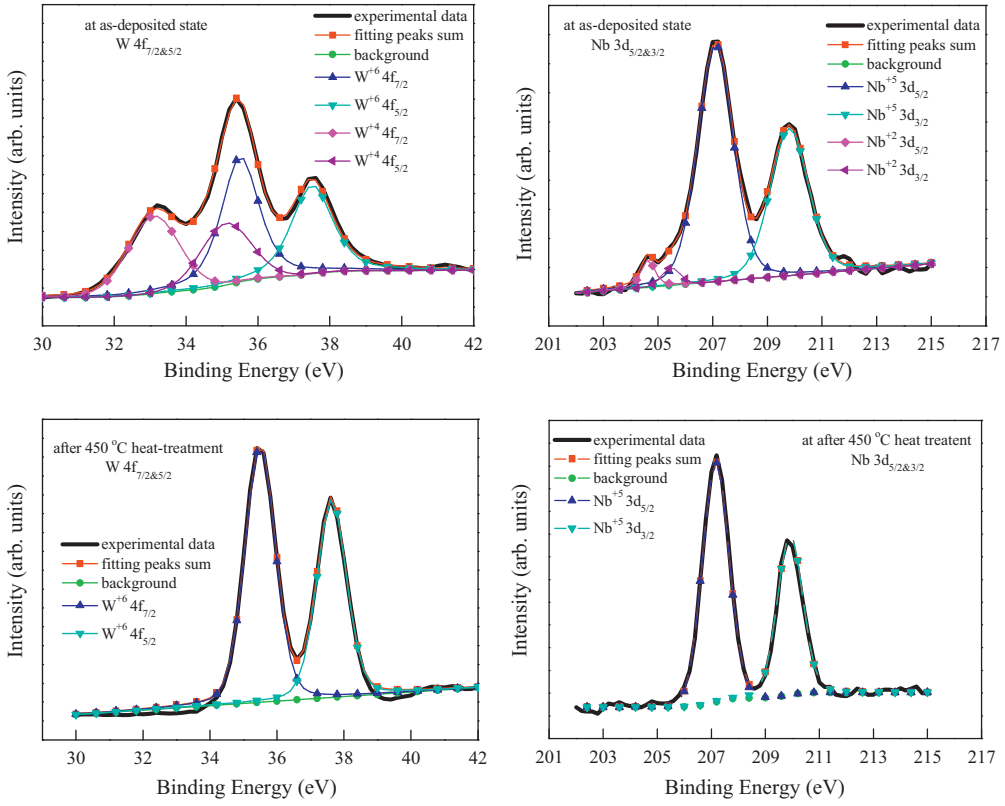

Fig. 4. The XPS spectra of W 4f7/2 and 5/2 and Nb 3d5/2 and 3/2 of Nb-doped WO_3 films at as-deposited and after heat treatment at 450 °C in O_2 atmosphere.

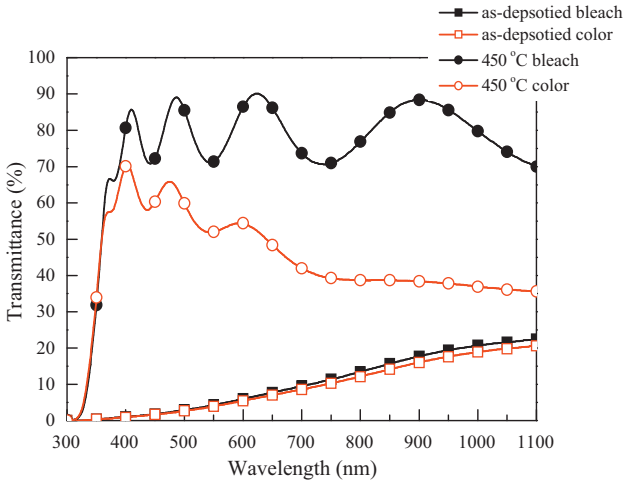

Fig. 5. The optical transmittance spectra of Nb-doped WO_3 film at as-deposited state and at heat-treated at 450 °C after bleach and color reaction.

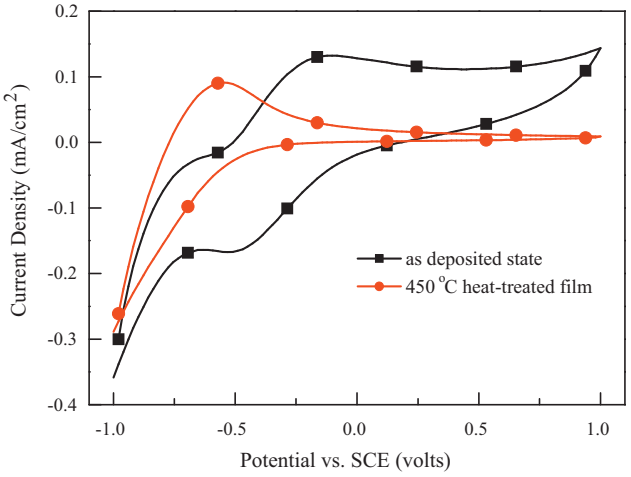

Fig. 6. The cycle voltammogram of electrochromic films for as-deposited state and 450 °C heat-treated of Nb-doped WO_3 films.

peak at 204.6 eV. Those XPS peaks are the superimposition of the doublets of Nb^{+5} (207.4, 209.7 eV) and Nb^{+2} (204.4, 206.3 eV) ions for Nb 3d5/2 and Nb 3d3/2 [27]. From those results, we can conclude that the chemical compositions in as-deposited Nb-doped WO_3 film are WO_2, WO_3, Nb_2O_5 and small amount of NbO. It can be inferred that the Nb atom reacts with oxygen of WO_3 to form NbO and Nb_2O_5. On the other hand, as XPS analysis was performed from the surface of 5 nm depth film, the exposure of Nb-doped film in air may be another reason for existence of large amount of Nb_2O_5. After annealing treatment at 450 °C in O_2 atmosphere the XPS spectra shows a W4f7/2 and 5/2 doublet at 35.4 and 37.6 eV and a doublet Nb 3d5/2 and 3/2 at 207.2 and 209.8 eV, which is stoichiometric chemical composition of WO_3 and Nb_2O_5. The as-deposited film and annealed film at 450 °C are colored at −1 V in $LiClO_4$/PC solution for 60 s.

The optical transmittance spectra of the films are shown in Fig. 5. In the coloration reaction, the W^{+6} ions are reduced into W^{+5} and the Nb^{+4} are reduced into Nb^{+4} to bring out the electrochromic effect. For the as-deposited film, the optical transmittance does not vary obviously before and after electrochemical insertion of Li^+ ions and the film color is still brown. The color of 450 °C annealed film becomes blue after Li^+ intercalation reaction at −1 V. The variation of optical transmittance at bleach and color state of as-deposited and 350, 400, and 450 °C annealed films are 0.6, 19, 35, and 38.4% at wavelength of 633 nm. The coloration efficiency of the films is calculated using the equation of CE = ΔO.D./ΔQ. The ΔO.D is the change of optical density and is equal to log(Tb/Tc), where Tb and Tc are the optical transmittance at bleach and color state at specific optical wavelength. ΔQ is the reacted charge density in the color or bleach reaction. The coloration efficiencies at 633 nm are 4, 18.5, 22, and 23 C/cm^2, respective for as-deposited film and 350, 400, and 450 °C annealed films. The increase of color efficiency with annealing temperature is due to chemical stoichiometry of electrochromic films.

Cyclic voltammetry (CV) were measured for as-deposited and 450 °C heat-treated films at the potential range of −1 to 1 V in three electrodes configuration with scan speed of 50 mV/s and the results are shown in Fig. 6. The CV loop of as-deposited film has a larger area compared to that of 450 °C annealed film and there are two pairs of cathodic/anodic current peaks. On the other hand, the 450 °C annealed film has only one pair of cathodic/anodic current peaks. However, in the Bathe's study,

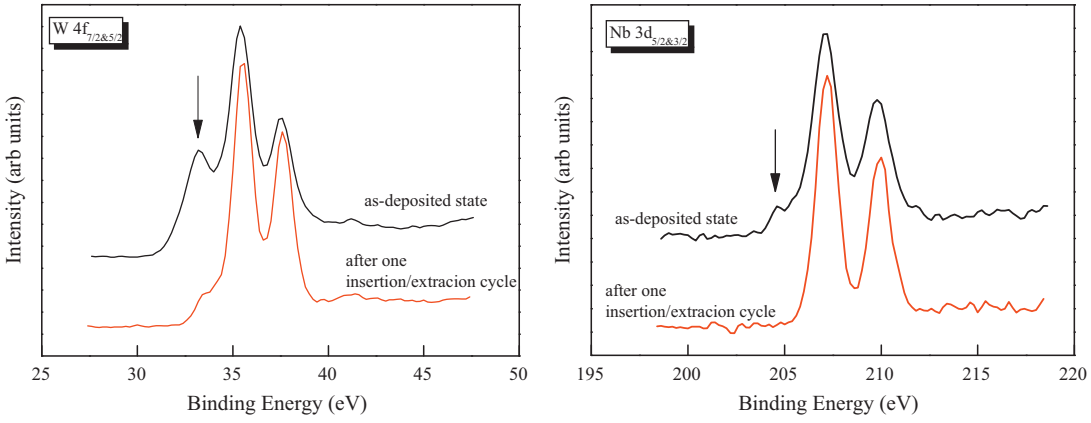

Fig. 7. The XPS spectra of W4f and Nb 3d of Nb-doped WO_3 films for as-deposited state and that after one insertion/extraction reaction.

they show only one pair of cathodic/anodic peak for 2% Nb–WO_3 films. In order to clarify the electrochemical mechanism in the insertion/extraction reaction, we compare the XPS spectra for as-deposited state and that after insertion/extraction cycle, which are shown in Fig. 7. It clearly shows that the peak intensity of W^{+4} and Nb^{+2} decrease after one insertion/extraction cycle. We can reasonably infer that those two pairs of cathodic/anodic peaks are consisted of the oxidation of WO_2 and NbO into WO_3 and Nb_2O_5.

4. Conclusion

The Nb-doping WO_3 electrochromic films are prepared successfully by electron beam method, where tungsten and niobium atoms are well distributed. The as-deposited film is amorphous and non-stoichiometric. The film does not show obvious electrochromic effect and in CV cycling the WO_2 and NbO are oxidized into WO_3 and Nb_2O_5. After post annealing in O_2 atmosphere, the film transforms into crystalline structure and become chemically stoichiometric. The energy band gap and electrochromic effect also increase with annealing temperature.

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