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Morphological and Electrochemical Properties of Cobalt-doped Nickel Oxide Thin Films

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ABSTRACT

The Morphological and electrochemical properties of undoped and cobalt (Co)-doped nickel oxide (NiO) thin films prepared on indium tin oxide (ITO)-coated glass substrates using a simple sol-gel spin-coating method were investigated. Both samples had compact and dense nanoparticle structures. The incorporation of Co dopant enhanced the electrochemical performance of NiO.

1 Introduction

Nickel oxide (NiO), a well-known transition metal oxide, has been studied for its morphological properties owing to its great potential application in optoelectronic and electrochemical devices [1-3].

In our previous study, we prepared nickel hydroxide ($Ni(OH)_2$) and NiO thin films using various preparation methods such as chemical bath deposition (CBD), sol-gel spin coating, and radio frequency (RF) magnetron sputtering for applications as anode electrode for electrochemical capacitors, buffer layer of organic photovoltaic (PV) cells, and anodically coloring electrochromic electrode, respectively [4-6].

In this study, we investigated the effect of cobalt (Co) dopant on the morphological and electrochemical properties of NiO thin films prepared using sol-gel spin-coating method, which was considered to be a relatively facile and cost-effective fabrication process.

2 Experiment

Undoped and Co-doped NiO thin films were prepared on indium tin oxide (ITO)-coated glass substrates using a sol-gel spin-coating method. The nickel and cobalt precursors were nickel acetate tetrahydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$, 0.5 or 0.4 M) and cobalt acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$, 0 or 0.1 M), respectively. The detailed fabrication processes were described in our previous studies [7-9]. The annealing treatment was performed at a temperature of 300 ºC for 1 h in air ambient. The heating rate was fixed at 2 ºC/min

The surface morphology was examined using field emission scanning electron microscopy (FESEM, JSM-6701F). Ultraviolet-visible-near infrared (UV-vis-NIR, UV-3600 Plus) transmittance spectra were measured in the wavelength range of 200 – 3000 nm. Electrochemical performances were investigated using cyclic voltammetry (CV, HOKUTO DENKO, HSV-100) with a potential range between −0.20 and +0.55 V versus Ag/AgCl reference electrode and Pt counter electrode in 1 M KOH aqueous electrolyte.

3 Results & Discussion

Figure 1 shows the FESEM images of NiO thin films prepared on ITO/glass substrates. As shown in Fig.1(a,d), the ~160-nm-thick-ITO thin film exhibited nanoparticle structures. From the cross-sectional images of undoped (Fig.1(b)) and Co-doped NiO (Fig.1(c)), the film thickness was approximately 100 nm. As shown in the FESEM images of undoped (Fig.1(b,e)) and Co-doped NiO

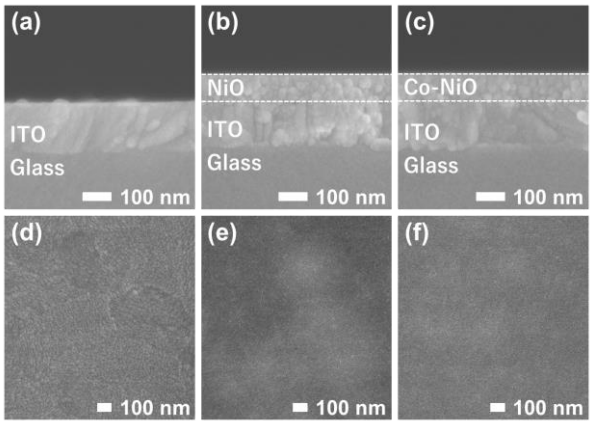

Fig.1. FESEM images of bare ITO/glass (a,d), undoped (b,e), and Co-doped NiO (c,f) thin film samples; cross (a-c) and (d-f) top-view.

(Fig.1(c,f)), both samples showed that particles, tens of nanometer in size, uniformly covered the surface of the ITO/glass substrates. In our previous study, the NiO thin film on the glass (Corning®

Eagle XG) and silicon substrates exhibited a compact and dense structure with a smooth surface devoid of cracks [7]. However, cracks were observed on the surface of the NiO thin films prepared on fluorine-doped tin oxide (FTO)-coated glass substrates. The incorporation of dopants (Co, Cu, and Zn) was found to decrease the number of cracks [8,9]. Whereas, both undoped and Co-doped NiO thin film samples prepared on ITO/glass substrates had compact and dense nanoparticle structures without noticeable cracks.

Figure 2 shows the UV-vis-NIR spectra of undoped and Co-doped NiO thin films prepared on ITO/glass substrates. As shown in the inset figures, the color changed from light grey and yellowish-brawn with incorporation of Co. In comparison with undoped NiO, the Co-doped NiO had a red-shifted absorption edge. The average transmittance values at a visible wavelength of undoped and Co-doped NiO thin film were ~80 and 74%, respectively. On the NIR region (780 – 2500 nm), the Co-doped NiO thin film exhibited slightly lower transmittance than that of undoped one. These results indicated that both samples could play the role of the anode buffer layer of PV cells without affecting absorption of the active layer.

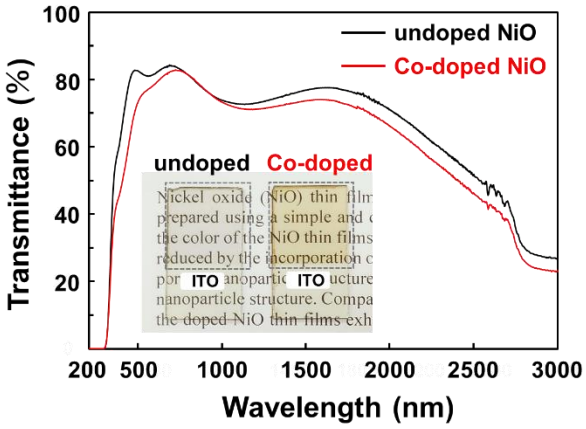

Fig.2. UV-vis-NIR spectra of undoped and Co-doped NiO thin films prepared on the ITO/glass substrates; Inset figures were photographs of the samples; the dotted square was a guide to the eye.

Figure 3 shows the CV curves of undoped and Co-doped NiO thin films as working electrodes at a scan rate of 50 mV/s in the potential range between –0.20 and +0.55 V. The effect of the ITO/glass substrate on the current density was negligible. Clearly, redox peaks were observed for both samples [10]. The intensities of the anodic and cathodic peaks increased with the incorporation of Co into NiO. It had similar tendency on the electrochemical performance of NiO thin film prepared on FTO/glass with corporation of Co dopant [8]. The inserted (Q_{in}) and extracted charge densities (Q_{ex}) of undoped and Co-doped NiO were calculated as 5.3 and -5.0 mC/cm^2 for undoped NiO and 9.9 and -9.5 mC/cm^2 for Co-doped NiO, respectively. The ratio of Q_{in} to Q_{ex} was approximately 1, suggesting that both samples had a highly reversible redox process. In addition, the colors of undoped and Co-doped NiO changed during CV cycling, indicating their suitability as anodically colored electrochromic electrodes.

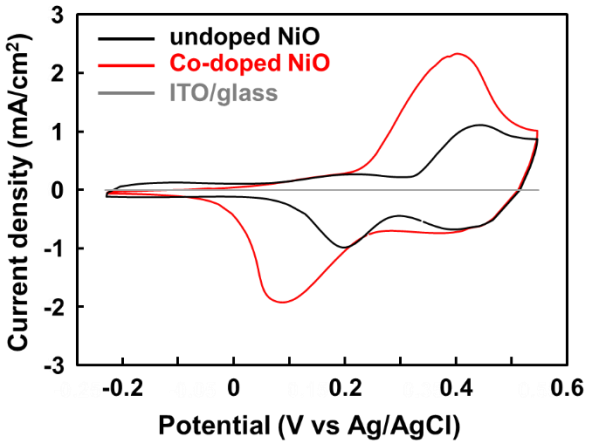

Fig.3. CV curves of undoped and Co-doped NiO thin films at a scan rate of 50 mV/s.

4 Conclusions

The NiO thin films were prepared on ITO/glass substrate using the sol-gel spin-coating method. Both undoped and Co-doped NiO thin films were composed of nanoparticles with a smooth surface morphology. The average transmittance of NiO thin film slightly decreased with the incorporation of Co. The electrochemical properties of the NiO thin film were enhanced by incorporating Co dopant.

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