EFFECT OF COBALT DOPANT ON THE CHARACTERISTICS OF NANOSTRUCTURED NICKEL OXIDE THIN FILMS

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Nickel oxide (NiO) thin films, incorporating Co dopant, were prepred by a simple sol-gel spin-coating method and their optical, morphological, and electrochemical properties were investigated and compared against undoped one. All the samples exhibit high transmittance in the visible wavelength region. The NiO and Co-doped NiO thin films, which are composed of nanoparticles, are compact and uniformly cover the surface of the glass substrates. Meanwhile, cracks are observed on the surface of the samples prepared on fluorine-doped tin oxide (FTO) coated glass substrates. The cracking is reduced by the incorporation of the Co dopant, as compared to undoped NiO. The surface morphology of the NiO thin film is effectively modified by substrate materials and dopant. Furthermore, the Co-doped NiO sample prepared on the FTO coated glass substrate exhibits a promising electrochemical performance with high-rate capabilities.

Key Words : *Nickel oxide, Dopant, Cobalt, Nanoparticle, Thin film*

1. INTRODUCTION

Among the many transition-metal oxides, nickel oxide (NiO) is a potential material for a wide range of applications, such as photovoltaic cells, electrochromic devices, electrochemical capacitors, and lithium-oxygen batteries [1-6].

Several NiO thin film preparation methods have been reported [1-8]. In a previous study, we introduced a novel sputtering technique combining effective substrate cooling with liquid nitrogen and water vapor as a reactive gas [2]. The metallic target mode is important to fabricate NiO thin films with a high deposition rate and exhibiting good electrochromic performance. We also studied the structural and electrical properties of Cu or Zn-doped NiO thin films prepared by sol-gel, which could provide a simple and cost-effective fabrication process [1,3,7]. The electrical properties and microstructures of the NiO thin films highly depend on the dopants.

This study discussed the optical, morphological, and electrochemical properties of a Co-doped NiO thin film and compared it with an undoped one.

2. EXPERIMENTAL

To prepare the undoped NiO sample, nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$, 0.5 M) was dissolved in 2-methoxyethanol (2ME, $C_3H_8O_2$). After stirring at 60 °C for 1 h, it was aged at room temperature for 24 h. After spin-coating, it was dried at 150 °C for 10 min, followed by annealing at 300 °C for 1 h. All thermal treatment was conducted in ambient air. To prepare the Co-doped NiO sample, nickel acetate tetrahydrate (0.4 M) and cobalt acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$, 0.1 M) were dissolved in 2ME. Then, the same dry and annealing procedures were carried out.

The optical transmittance properties were investigated using ultraviolet-visible (UV-Vis.) spectroscopy (HITACHI, U-2910). The surface mor-

phology was analyzed with field emission scanning electron microscopy (FESEM, JSM-6701F). Using a typical three-electrodes system (HOKUTO DENKO, HZ-7000), the electrochemical properties of the prepared NiO and Co-doped NiO thin film samples were investigated using cyclic voltammetry (CV) in 1 M KOH aqueous electrolyte at a potential range of between −0.25 and +0.55 V versus Ag/AgCl reference electrode.

3. RESULTS AND DISCUSSION

The effect of high amounts of incorporated Co dopant on the properties of the NiO thin film has rarely been reported [8]. From the XRD (X-ray diffraction) and FTIR (Fourier transform infrared spectroscopy) results (not shown in here), it was confirmed that the prepared thin film samples are single-phase nanocrystalline NiO.

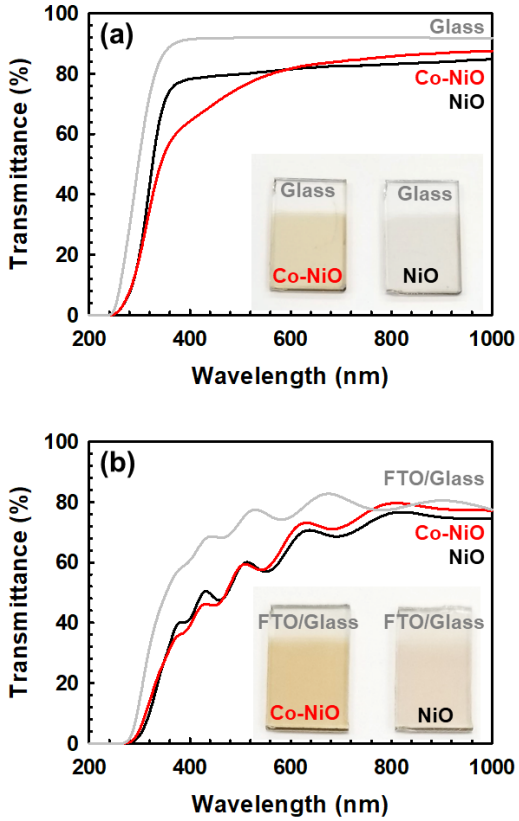

Fig.1. Transmittance spectra of NiO and Co-NiO thin films prepared on glass (a) and FTO coated glass (b) substrates. Inset figures are photographs of the samples.

Figure 1 shows the transmittance spectra of NiO and Co-doped NiO thin films prepared on glass (a) and fluorine-doped tin oxide (FTO) coated glass (b) substrates with the insets showing photographs of the samples. The NiO and Co-doped NiO samples prepared on the glass substrates exhibit high transmittance in the visible wavelength region, averaging approximately 80% and 76%, respectively. Meanwhile, due to the thick FTO film (thickenss ~550 nm), both samples prepared on the FTO coated glass substrates have a relatively low transmittance as compared to the ones prepared on glass substrates. The NiO sample is light grey and the Co-doped NiO sample is slightly reddish.

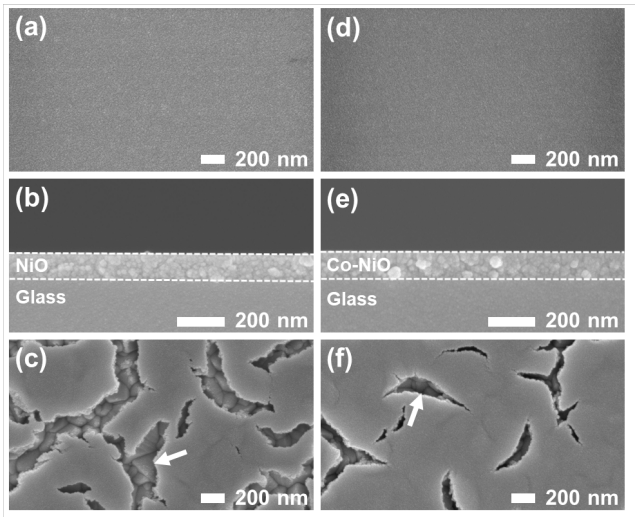

Fig.2. FESEM images of NiO (a-c) and Co-doped NiO (d-f) thin films prepared on different substrates; (a,c,d,f) top images and (b,e) cross-sectional images; and (a,b,d,e) glass and (c,f) FTO coated glass.

Figure 2 shows the cross-sectional FESEM images of the NiO thin films without (a-c) and with (d-f) Co dopant. Figure 2(a,d) shows that particles, tens of nanometers in size, uniformly cover the surface of the glass substrates. All samples exhibit compact and dense thin film with a smooth surface devoid of cracks. Additionally, the thin films prepared on the silicon wafer substrate have a similar morphology. The film thickness is approximately 120 nm (Fig. 2(b,e)). Meanwhile, the film uniformity of the NiO and Co-doped NiO samples prepared on the FTO coated glass substrates is different. Figure 2(c,f) shows that the crack density, indicated by arrows, slightly decreases with the incorporation of the Co dopant. A similar tendency was observed in the NiO thin film with Zn dopant [3]. The incorporation of dopant may have released the residual stress of the NiO thin film [9].

The charge response performacne of the electro-

chemical capacitors to a varying voltage was evaluated by the CV curve [10]. After exposing the samples prepared on the FTO coated glass substrates to ozone, the CV measurement was carried out.

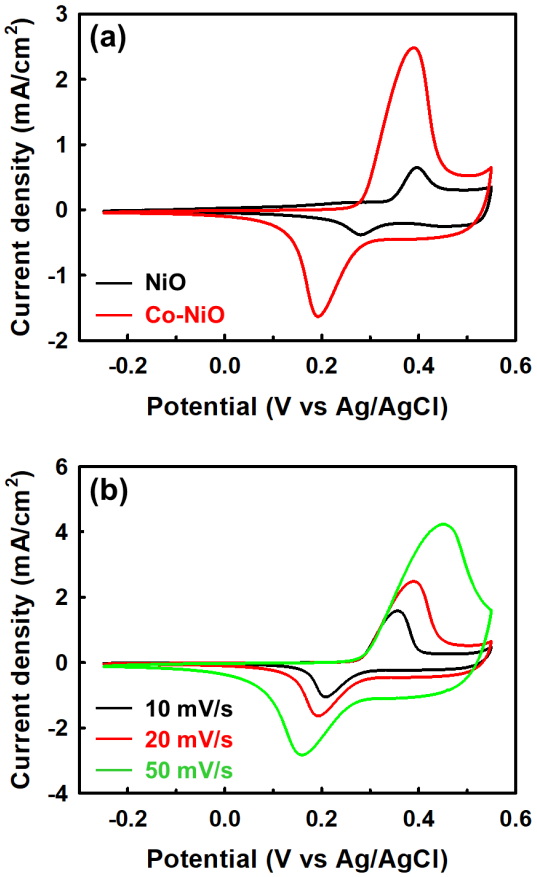

Fig.3. CV curves of the NiO and Co-doped NiO samples at a scan rate of 20 mV/s (a) and Co-doped NiO sample at various scan rates (b).

Figure 3(a) shows the CV curves of the NiO and Co-doped NiO thin films at a scan rate of 20 mV/s. The effect of the FTO coated glass substrate on the current density is negligible [11]. The CV curves of both samples show a pair of strong anodic and cathodic redox peaks, mainly originating from the oxidation reaction of Ni^{2+} to Ni^{3+} and its reverse reduction reaction [4]. Meanwhile, the incorporation of Co dopant shifts the redox peaks to lower potential. A similar tendency was observed on the Ni-Co hydroxide sample with an increase in the Co/Ni ratio [12]. The Co-doped NiO sample possesses a larger integral area and redox current density as compared to the undoped one.

Figure 3(b) shows the CV curves of the Co-doped NiO sample at various scan rates. As the scan rate increases, the shape of the CV curves is well maintained and the area under the curve proportionally increases. The areal specific capacitance (C) is calculated according to the following equeation [4,6]:

$$C = \frac{1}{2av\Delta V}\int I(V)dV$$

where a is the active electrode area, v is the scan rate, and ΔV is the applied potential window. The calculated C is approximately 19.4, 18.6, and 17.0 mF/cm^2 at 10, 20, and 50 mV/s, respectively. The Co-doped NiO sample exhibits excellent high-rate capabilities with an increasing scan rate [13]. It also shows a better performance than other transition oxide material [10]. No peeling-off on the surface of the NiO and Co-doped NiO thin films was observed after the CV measurement, even though numerous cracks were observed on the both samples.

4. CONCLUSIONS

NiO thin films were prepared by a low cost and simple preparation process: the sol-gel spin-coating method. Incorporation of Co dopant on the NiO provides an effective way to modify the optical transmittance and surface morphology. The Co-doped NiO thin film prepared on FTO coated glass substrate has strong redox peaks due to the Faradic reaction and exhibits a promising electrochemical performance as supercapacitors.

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