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Kim Kyung Ho, Takahashi Chiaki, Abe Yoshio, Kawamura Midori

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Effects of Cu doping on nickel oxide thin film prepared by sol-gel solution process

Kyung Ho Kim*, Chiaki Takahashi, Yoshio Abe, Midori Kawamura

Department of Materials Science and Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan

Abstract

We prepared nickel oxide (NiO) thin films with p-type Cu dopants (5 at%) using a sol-gel solution process and investigated their structural, optical, and electrical characteristics by X-ray diffraction (XRD), atomic force microscopy (AFM), optical transmittance and current-voltage (I-V) characteristics. The crystallinity of the NiO films improved with the addition of Cu dopants, and the grain size increased from 38 nm (non-doped) to 50 nm (Cu-doped). The transmission of the Cu-doped NiO film decreased slightly in the visible wavelength region, and the absorption edge of the film red-shifted with the addition of the Cu dopant. Therefore, the width of the optical band gap of the Cu-doped NiO film decreased as compared to that of the non-doped NiO film. The resistivity of the Cu-doped NiO film was 23 Ω·m, which was
significantly less than that of the non-doped NiO film (320 Ω·m). Thus, the case of Cu dopants on NiO films could be a plausible method for controlling the properties of the films.

Keywords: NiO, Cu dopant, Sol-gel, Crystallinity, Optical band gap, Resistivity

Corresponding author: Kyung Ho Kim, Tel: 81-157-56-9431, Fax: 81-157-26-4973,
E-mail address: k hkim@mail.kitami-it.ac.jp
1. Introduction

Wide band gap semiconducting nickel oxide (NiO) thin films have attracted considerable attention because of their low material cost, excellent durability, and electrochemical stability in a broad range of applications such as gas sensors, electrochromic (EC) devices, organic light-emitting diodes (OLEDs), and organic photovoltaic (OPV) cells [1-4]. Several methods for preparing NiO thin films have been introduced, such as the thermal evaporation, sputtering, pulsed laser ablation, electrochemical deposition, and sol-gel methods [5-10]. Among these methods, the sol-gel solution process provides the advantages of high purity of the raw materials, easy control of the composition, and a homogeneous solution [11-13].

In our previous study, we reported the properties of NiO films fabricated using a sol-gel spin-coating method and their application as the anode buffer layer of OPV cells [14]. The surface roughness and optical band gap were strongly related to the film thickness [14]. The electrical properties of the NiO buffer layer played an important role in improving the performance of OPV cells [14]. However, the electrical resistivity of the NiO films with sol-gel solution process was relatively high as compared to that of the films prepared by other vacuum processes [15].

On the other hands, it is well known that the characteristics of NiO films strongly
depend on the dopants (Au, Fe, Li, or Cu) added to the films [16]. In this study, we investigated the structural, optical, and electrical properties of Cu-doped NiO films prepared by sol-gel solution process.

2. Experimental

NiO thin films were prepared using the sol-gel solution process with Cu dopant. The nickel acetate tetrahydrate (Ni(COOCH₃)₂·4H₂O, 0.3 M) precursors were dissolved in 2-methoxyethanol (2ME), and hydrochloric acid (HCl) was added as catalyst [10,14]. Copper acetate monohydrate (Cu(CH₃COO)₂·H₂O, 5 at%) was used as the dopant. The solution was stirred at 60 °C for 1 h and then aged for 24 h at room temperature. The glass substrates were subjected to a standard cleaning process with acetone, isopropyl alcohol, and deionized water for 10 min each, in an ultrasonic bath. After the sol was spin-coated on the glass substrates, the films were annealed at 550 °C for 1 h in air in a furnace with a heating rate of 10 °C/min. The thickness of the NiO thin film was fixed at 60 nm.

The structure of the Cu-doped NiO films was examined by performing X-ray diffraction (XRD, Bruker, D8ADVANCE) measurements with a Cu Kα radiation source (λ) of 0.15406 nm. The surface morphology was investigated using atomic force
microscopy (AFM, SHIMADZU, SPM-9500J3). The optical properties were investigated by performing ultraviolet-visible (UV-vis) spectroscopy (HITACHI, U-2910). Two-point probe current-voltage ($I$-$V$) measurements for the Cu-doped NiO films were conducted using a Keithley 2400 source meter at room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the non-doped and Cu-doped NiO films on glass substrates. The film shows XRD peaks at 37.2° and 43.3°, which correspond to the (111) and (200) crystal planes, respectively, of the cubic NiO phase (JCPDS Card No. 4-0835) with a lattice constant ($a$) of 0.41769 nm. However, no extra diffraction peaks corresponding to metallic Zn or Cu or to copper oxide (CuO) were observed, which may be because the ionic radii of Ni (0.078 nm) and Cu (0.082 nm) are very similar; Cu ions can be easily substituted for Ni ions without significant lattice distortion [17,18]. The variation of lattice constant is listed in Table 1. It is also noticeable that the intensity of the crystalline peaks of the Cu-doped NiO film progressively improved and the full width at half maximum (FWHM) of the peaks narrowed as compared to that of the non-doped NiO film, indicating better crystal quality. The average particle sizes calculated according to the Scherrer’s formula [19]
were 30 nm for the non-doped NiO film and 38 nm for the Cu-doped NiO film.

The effect of the Cu dopant on the surface morphology of the NiO films was investigated by AFM in the tapping mode. As shown in Fig. 2, the surface of the non-doped and Cu-doped NiO films were uniform and without voids over the entire substrate. The particle sizes of the non-doped and Cu-doped NiO films were 38 nm and 50 nm, respectively, which is well consistent with the XRD results. The root mean square (RMS) roughness is approximately 1.75 nm for the non-doped film and 2.23 nm for the Cu-doped NiO film. Thus, the value of RMS roughness slightly increases with the increase in the grain size with Cu doping.

Figure 3(a) shows the transmittance spectra of the non-doped and Cu-doped NiO thin films on glass substrates. The average transmission of the Cu-doped NiO film decreases in the visible region owing to an increase in the scattering resulting from rough surface morphology of the Cu-doped NiO film. It is also seen that the absorption edge is red-shifted to the visible region with Cu doping, which indicates the narrowing of the optical band gap. As shown in Fig. 3 (b), the band gap of the non-doped NiO, as determined from the intercept on the energy axis of the linear portion of \((\alpha h v)^2\) versus \(h v\), is 3.73 eV, which is in good agreement with the reported band gap value for NiO films prepared by other methods [7, 17]. The decrease in the
value of the optical band gap of the Cu-doped NiO film to 3.69 eV may be attributed to the improvement in the crystalline quality of the films as well as to the increased in the grain size [20].

Two-point current-voltage (I-V) measurements were carried out to obtain the electrical resistivity of non-doped and Cu-doped NiO films; the results are shown in Fig. 4. All curves show a linear I-V relationship within a certain voltage. The electrical resistivity calculated from the linear part of the experimental data by linear fitting. The resistivity decreased from 320 Ω·m for the non-doped film to 23 Ω·m for the Cu-doped film because large numbers of Ni ions were replaced by Cu ions and occupied interstitial sites in the NiO lattice [17,18,21].

4. Conclusions

The effects of a p-type Cu dopant (5 at%) on the structural properties, surface morphology, optical transparency, and electrical resistivity of a NiO films were investigated. The structure of the NiO films was random-oriented and the addition of the Cu dopant increased the grain size, which influenced the surface morphology and transmission of the NiO films. The optical band gap value of the Cu-doped NiO film (3.69 eV) was lower than that of the non-doped NiO film (3.73 eV). The resistivity of
the Cu-doped NiO film was 23 $\Omega\cdot$m, which was significantly less than that of the non-doped NiO film (320 $\Omega\cdot$m).

**Acknowledgement**

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References


**Figure captions**

Fig. 1. XRD patterns of non-doped and Cu-doped NiO films on glass substrates.

Fig. 2. AFM images of non-doped (a-c) and Cu-doped (d-f) NiO films in three (a, d) and two (b, e) dimensions and their height profiles (c, f).

Fig. 3. (a) UV-vis transmittance spectra and (b) plots of \((\alpha h \nu)^2\) versus \(h \nu\) for NiO thin films.

Fig. 4. Current–voltage (I-V) curves of NiO thin films.
Table 1. Information obtained from XRD patterns for non-doped and Cu-doped NiO films.

<table>
<thead>
<tr>
<th></th>
<th>hkl</th>
<th>$\theta$ (deg.)</th>
<th>d-spacing (nm)</th>
<th>*Lattice parameter, a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-doped</td>
<td>111</td>
<td>37.26</td>
<td>0.24113</td>
<td>0.41763</td>
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<tr>
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<td>200</td>
<td>43.30</td>
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<td>0.41758</td>
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<tr>
<td>Cu-doped</td>
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<td>0.24088</td>
<td>0.41720</td>
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<tr>
<td></td>
<td>200</td>
<td>43.32</td>
<td>0.20870</td>
<td>0.41740</td>
</tr>
</tbody>
</table>

* $a = d\sqrt{h^2 + k^2 + l^2}$
Fig. 1.
Fig. 2.
Fig. 3.

(a) Transmittance (%) vs Wavelength (nm) for Glass, Cu 0 at%, and Cu 5 at%.

(b) $(\alpha h \nu)^2 \times 10^{11} \text{cm}^{-1} \text{eV}^{-2}$ vs Energy (eV) for Cu 0 at% and Cu 5 at%.
Fig. 4.