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Preparation of transparent and conductive ZnO films using a chemical solution deposition process

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Transparent ZnO films were prepared by a chemical solution deposition process using an Al/Ni/Zn organic solution. Spin-coated film was amorphous, but the film annealed at 500°C showed a Wurtzite ZnO structure and (002) preferred orientation. The thicknesses of the films were 0.09-0.15 μm for 5-times coating and 0.2-0.3 μm for 10-times coating. The transmittance of the films was 43-97% in the visible light region (400-800 nm). An abrupt increase in the absorption occurred below 380 nm. The electrical resistivity of the as-produced ZnO films was greater than 50 Ω cm. A heat-treatment of the film in hydrogen decreased the electrical resistivity to 0.37 Ω cm. Ni-doped (2 mol%)ZnO films showed a lower electrical resistivity (0.14 Ω cm). The electrical resistivity of this film became lower still by the addition of Al to about 0.03 Ωcm (Ni(2 mol%)/Al(1 mol%)/ZnO). But higher Al-doped Ni(2 mol%)/Al(3 mol%)/ZnO films showed a higher electrical resistivity (about 0.25 Ω cm) than Ni(2 mol%)/ZnO film.

Key words: ZnO, Film, Transparency, Electrical resistivity, Band gap, Al, Ni.

Introduction

ZnO films have been used as electrical ceramic materials because of their interesting electrical and optical properties. For example, ZnO films have been practically used as transparent electrodes for many devices such as surface acoustic waves (SAW), and gas sensors [1].

Although a merit of transparent conductive ZnO film is lower cost than the mainly used ITO (Sn doped In_2O_3) films, several problems in ZnO films, such as the instability of properties in the atmosphere and the large change of electrical conductivity with temperature, have been pointed out [1]. Studies to improve the heat-resistance and conductivity by substituting Zn sites with group III or IV elements have been performed recently by many processes [2-5]. The conductivity of Al-doped ZnO film was improved also by annealing in a hydrogen atmosphere [6]. Also, a Ni-doped ZnO film showed higher electrical conductivity [7].

In this paper, we report the preparation and properties of transparent ZnO films prepared by a spin-coating method using an Al/Ni/Zn organic solution.

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Experimental Procedure

Preparation

Figure 1 shows the experimental procedure for preparing ZnO films. The composition of films were $97ZnO \cdot 3Al_2O_3$ and $(98\text{-}x)ZnO \cdot 2NiO \cdot xAl_2O_3$, where x = 0-3. Zinc acetate, aluminium nitrate, and nickel nitrate were used as metal sources. These salts and diethanolamine were mixed with ethanol at the above compositions. The resulting solution was allowed to stand at 60°C for 30 minutes whilst stirring. The molar ratio of diethanolamine to zinc acetate was fixed at 1.0 and the concentration of zinc acetate was fixed at 0.25 mol/l.

The film was formed on a transparent quartz glass plate by a spin coating method (1000 rpm, 30s). The films were annealed at 300°C for 1h in air. This procedure was repeated 4 or 9 times. After the fifth or tenth coating, the films were heat-treated at 500°C. Then, some of the films were annealed at 450°C for 1h in a hydrogen atmosphere.

Characterization

The phases of the ZnO film were identified by X-ray diffractometer (XRD) using CuKα radiation. The optical properties were evaluated by UV-VIS. The electrical conductivity was measured by the Van der Pauw method [8]. The surface and cross-section of the films were observed by scanning electron microscope (SEM).

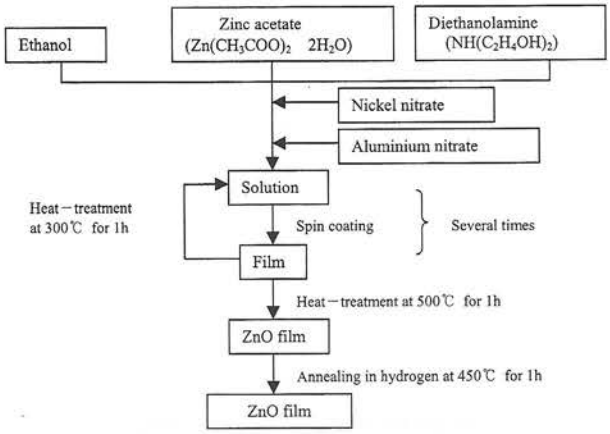

Fig. 1. Procedure for ZnO films preparation.

Results and Discussion

Phase

The as-coated films were amorphous, but the heat-treated films showed the Wurtzite ZnO structure. Figure 2 shows XRD patterns of the films annealed in hydrogen. The resulting films showed the Wurtzite ZnO crystal pattern. The peak ratio of (002)/(101) planes of the ZnO film was 95/100 and this value is higher than that of JCPDS ZnO(36-1451), 44/100. This means that the ZnO films in this work showed (002) preferred orientation. The Al-doped ZnO films showed broad diffraction peaks, and these peaks became lower with increasing Al content (Fig. 2(c) → (d) → (e)). This may be due to the inhibition of ZnO grain growth by the precipitated Al_2O_3.

Optical transmittance and Band gap

The optical transmittance of pure and Al, Ni-doped ZnO films are given in Figs. 3 and 4. All films before annealing in hydrogen were highly transparent in the visible region. Ni-doped ZnO films annealed in hydrogen, however, showed lower transmittance. This decrease in transmittance may be due to the deposition of Ni metal in the film since nickel oxide is easily reduced to nickel metal by hydrogen.

Generally, the absorption of light occurs when the electrons in a valence band are activated up to a conduction band. The band gap between them can be estimated by the following equation:

$$\alpha \propto \frac{(h\nu - Eg)^{1/2}}{h\nu} \quad (1)$$

where α is the absorption coefficient, Eg is the band gap, and $h\nu$ is the photon energy. A linear relation between the $(\alpha h\nu)^2$ and $(h\nu)$ values is obtained, and the extrapolation of the line $((\alpha h\nu)^2 = 0)$ gives Eg values as shown in Fig. 5(a) and (b). The band gaps obtained of ZnO are listed in Table 1. The band gap of pure ZnO was 3.274 eV and this value is close to another value in the literature, 3.26 eV [9]. Al-doping of ZnO increased the band gap, but Ni-doping decreased it. The increase in the band gap on Al-doping may be due to the Burstein-Moss shift [10], in which the apparent band

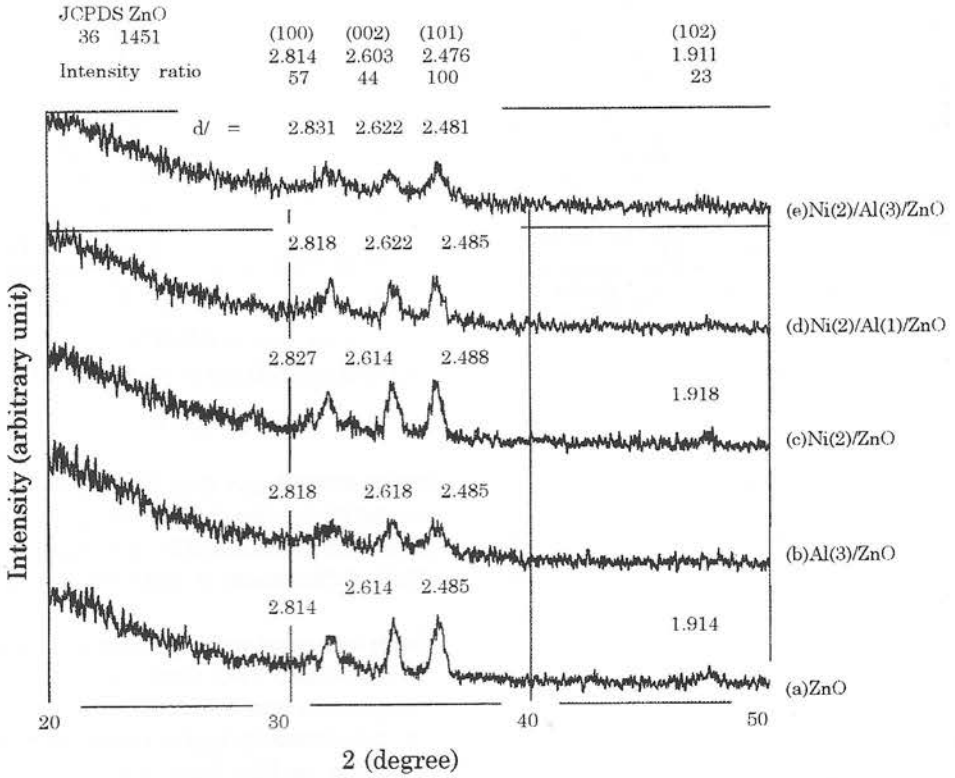

Fig. 2. X-ray difrraction patterns of pure ZnO and Al- and and/or Ni-doped ZnO thin films.

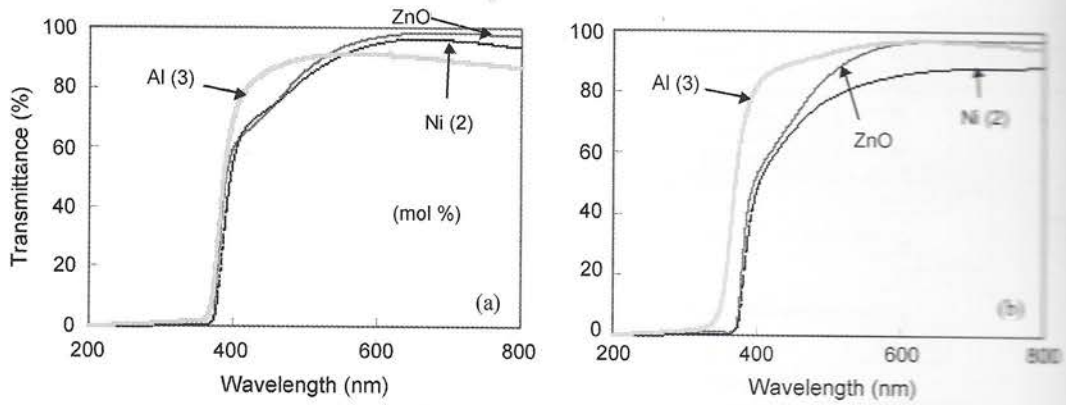

Fig. 3. Optical transmittance spectrum for ZnO, and Ni- or Al-doped ZnO films (a) before and (b) after annealing in hydrogen.

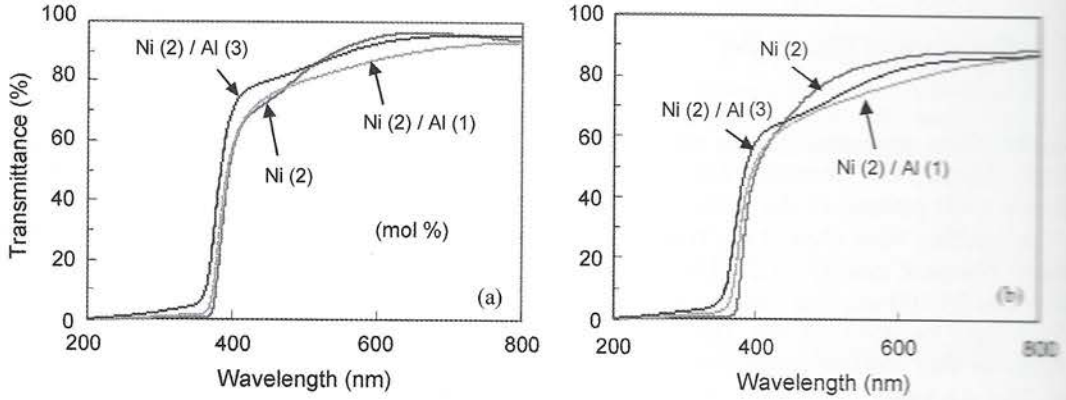

Fig. 4. Optical transmittane spectrum for Ni-doped ZnO and Ni-Al-doped films (a) before and (b) after annealing in hydrogen.

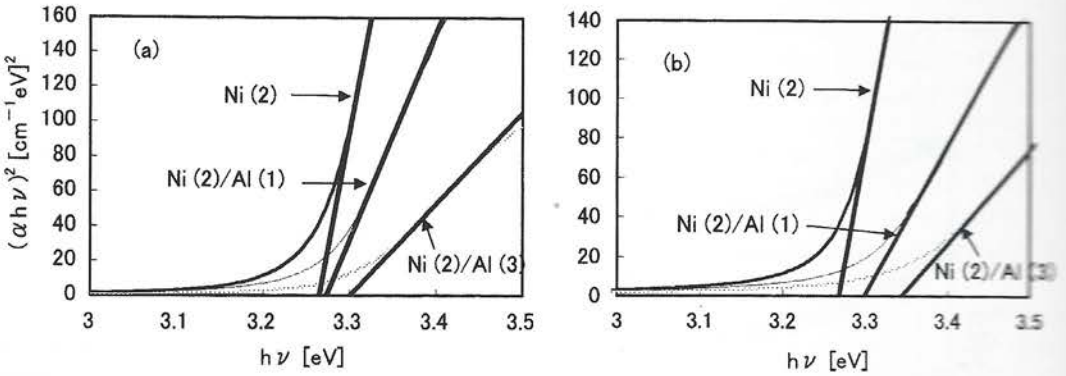

Fig. 5. $(\alpha h\nu)^2$ versus $h\nu$ curves for the band gap determination in (a) ZnO, and Al-doped ZnO and (b) Ni-doped ZnO and Al-Ni-doped ZnO films annealed at 450°C in hydrogen.

Table 1. The band gaps of ZnO annealed in atmosphere and hydrogen

Samples	Band gap (eV)	
	Atmosphere	Hydrogen
ZnO	3.274	3.274
Al(3)/ZnO	3.284	3.289
Ni(2)/ZnO	3.266	3.268
Ni(2)/Al(1)/ZnO	3.273	3.299
Ni(2)/Al(3)/ZnO	3.300	3.344

gap becomes larger than the original one because of the occupation of the bottom of the conduction band by carrier electrons. On the other hand, the reason for the effect of Ni-doping is under investigation.

Electrical conductivity measurements

As-produced ZnO films showed an electrical resistivity, greater than 50 Ω cm. The treated film in hydrogen gas, however, had a smaller resistivity, 0.57 Ω cm as shown in Fig. 6(a). ZnO is a non-stoichiometric compound [11] and tends to have a Zn-rich compo-

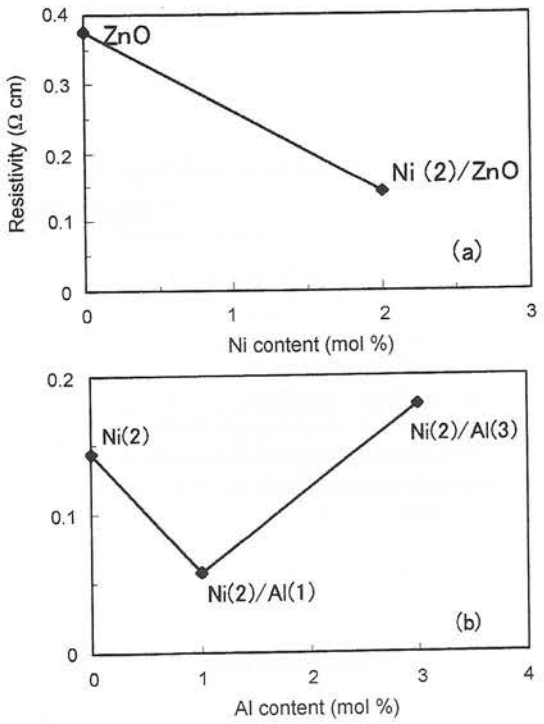

Fig. 6. The change in resistivity with (a) increasing of Ni content, and with (b) increasing of Al content.

tion, $Zn_{1+\delta}O$, as shown in the following equation under hydrogen treatment. According to this equation, the formation of an interstitial Zn ion accompanies an electron. This must increase the conductivity of the ZnO film in this work.

$$Zn_{Zn}^{\times} + O_o^{\times} \rightleftarrows Zn_i^{\cdot} + 1/2O_2(g) + e \qquad (2)$$

Ni-doped (2 mol%) ZnO films (Fig. 6(a)) showed lower electrical resistivity (0.14 Ω cm).

The addition of Al to this film lowered the electrical resistivity to about 0.03 Ω cm (Ni(2 mol%)/Al(1 mol%)/ZnO) (Fig. 6(b)). Although the solubility of Al_2O_3 in ZnO is very small, 2.13×10^{-5} mol% [12], a small amount of the substituted Al generates electrons as shown in the following equation. This decreased the electrical resistivity of the ZnO film in this work.

$$Al_2O_3 \overset{ZnO}{\rightleftarrows} 2Al_{Zn}^{\cdot} + 2O_o + 1/2O_2(g) + 2e \qquad (3)$$

The higher Al-doped Ni(2 mol%)/Al(3 mol%)/ZnO films showed higher electrical resistivity (about 0.25 Ω cm) than the Ni(2 mol%)/ZnO film. This must be due to the formation of Al_2O_3 insulating layer between the ZnO grains.

Microstructure

Figure 7 shows SEM photographs of (a) as-produced ZnO, (b) hydrogen-treated ZnO, and (c) hydrogen-treated Ni(2 mol%)/Al(1 mol%)/ZnO films. The films consisted of small ZnO grains. The grain size of the film treated in hydrogen gas was larger than that of as-produced one (Fig. 7(a), (b)). But the grain size of the Ni-doped film was small (Fig. 7(b), (c)) and the surface was very smooth.

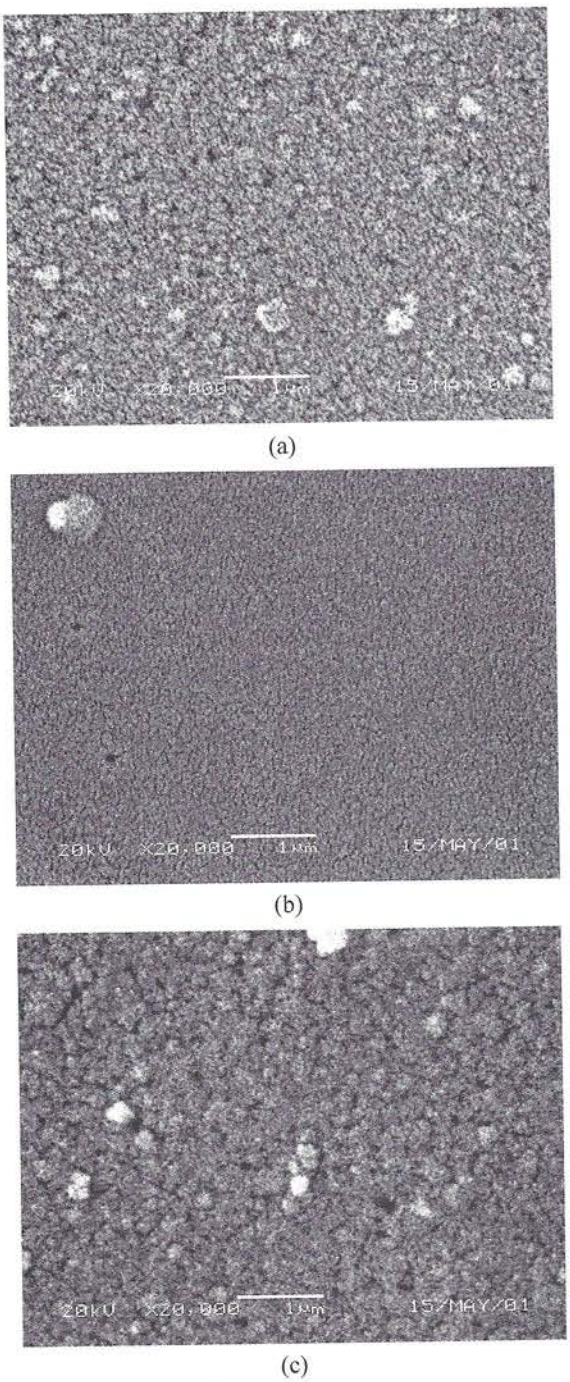

Fig. 7. SEM photographs of (a) as-produced ZnO, (b) hydrogen-treated ZnO, and (c) hydrogen treated Ni(2)/Al(1)/ZnO film (⊢⊣ 1 μm).

Conclusions

Transparent and conductive ZnO films were prepared by a chemical solution deposition process. The follow-

ing factors are found to be important in this process, (1) Annealing in hydrogen, (2) the addition of NiO and Al_2O_3. The higher addition of NiO and Al_2O_3 decreased the transparency and the conductivity, respectively.

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