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Fabrication of *p*-Type Li-Doped ZnO Films by RF Magnetron Sputtering

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The *p*-type Li-doped ZnO films are successfully deposited on a glass substrate by RF magnetron sputtering at room temperature. The pure, crystalline sputtering target of $Li_XZn_{1-X}O_{1-X/2}$ with X in the range of 0–0.003 is fabricated using the powder synthesized by the thermal decomposition of a metal–nitrate–tartrate gel complex at 400°–800°C. The complex is prepared by dissolving nitrates of zinc and lithium in an aqueous solution with nitric and tartaric acids. The resulting compacts, which can be densified at 1400°C, exhibit a decreasing trend of electrical resistivity with increasing Li content. For the composition with 0.2 mol% Li, the *p*-type Li-doped ZnO film has an electrical resistivity of 1.3 $\Omega\cdot$cm, Hall mobility of 0.77 $cm^2\cdot(V\cdot s)^{-1}$, carrier concentration of 6.67×10^{18} cm^{-3}, and high optical transmittance in the visible region.

I. Introduction

Zinc oxide film, which is optically transparent, can be made *n*-type conductive by doping Al,[1] or *p*-type by N, P, and As.[2–4] However, these dopants suffer from achieving low-resistivity *p*-type ZnO films due to self-compensation, deep acceptor level, and low solubility of the acceptor dopants.[5] Recently, Zeng *et al.*[6] and Xiao *et al.*[7] demonstrated that *p*-type ZnO film could be made by doping Li using dc reactive magnetron sputtering (dc-RMS) and pulsed laser deposition (PLD) methods, respectively. The Li-doped ZnO target, which is fabricated using the powders prepared by a solid-state reaction of Li_2CO_3 and ZnO, easily results in a nonuniform distribution of Li, forming an undesirable crystalline phase of Li_2O at high-temperature calcination. This gives rise to poor electrical properties of the as-deposited films. Moreover, the evaporation of Li_2O easily occurs because both dc-RMS and PLD methods involve high-temperature process. This occasionally changes the electrical characteristics of Li-doped ZnO films from *p*-type to *n*-type conduction, creating processing uncertainty. To solve the above problems, the pure, crystalline target of $Li_XZn_{1-X}O_{1-X/2}$ with X in the range of 0–0.003 is prepared using the powder synthesized by a soft-chemical-reaction route,[8–10] and the results are compared with those prepared by a conventional solid-state reaction method. The Li-doped ZnO films are fabricated by the RF magnetron sputtering method at room temperature to minimize the potential evaporation loss of Li ion during vacuum deposition.

II. Experimental Procedure

$Li_XZn_{1-X}O_{1-X/2}$ with X in the range of 0–0.003 powders were synthesized by soft-chemical- and solid-state-reaction methods. For the solid-state reaction method, powders of Li_2CO_3 (Merck, Rahway, NJ) and ZnO (Showa, Tokyo, Japan) were weighed according to the stoichiometric ratio of each cation and mixed by ball milling in 1-propanol. The mixture was dried at 90°C for 24 h, and then calcined at 400°–800°C for 2 h to remove carbonates. To fabricate sputtering targets, the green compact was fired at 1400°C for 2 h in air. For the soft-chemical-reaction method, an aqueous solution was prepared by dissolving 0–0.003*M* $LiNO_3$ (J. T. Baker, Phillipsburg, NJ), 0.997–1*M* $Zn(NO_3)_2\cdot6H_2O$ (RDH, Munich, Germany), 1*M* tartaric acid (Riedel-de Haen, Milan, Italy), and 2 N HNO_3. The clear yellow solution was heated under stirring at 80°C until it appeared dry. To remove water completely, the gel complex was dried at 155°C for 1 h. The resulting brown powder was then calcined at 400°–800°C for 2 h in air. The crystallinity of the calcined powders was confirmed by X-ray diffraction (PW-1700, Philips, Eindhoven, the Netherlands) analysis. The calcined powder was ball-milled in 1-propanol for 48 h, and the resulting powder had a median particle size of 0.06–0.08 μm (JEM-2100F, Tokyo, Japan). The ground powder was then mixed with 5 wt% poly (ethylene glycol) binder in 1-propanol. The suspension was deagglomerated by a high-energy ultrasonic horn, and mixing was continued in a high-speed mixer (Maschinenfabrik, Basel, Switzerland) for 2 h. The powder mixture was dried, ground, and uniaxially pressed at approximately 90 MPa to produce pellets of 1.0 cm diameter and 0.1 cm thickness. The density of the green compacts was measured dimensionally, and the results were in the range of 50%–52% of the theoretical density. The samples were fired at a heating rate of 1°C/min from room temperature to 500°C, which was maintained for 60 min to remove the binder. After binder burnout, the samples were sintered isothermally in air at 1400°C for 2 h. The densities of the sintered compacts were measured by the water replacement method. The crystalline phases of the sintered samples were identified by XRD analysis. The microstructure of the fired composites was observed from fracture and top surfaces using a field-emission scanning electron microscope (FE-SEM; LEO1530, Oberkochen, Germany). The electrical conductivities of densified $Li_XZn_{1-X}O_{1-X/2}$ samples were measured at room temperature in air using a standard four-probe technique, and a platinum electrode was used to minimize the interfacial interaction between electrode and ceramics.

$Li_XZn_{1-X}O_{1-X/2}$ films with $X=0$ and 0.002, which were fabricated using the target prepared by the soft-chemical-reaction-derived powder, were deposited on the glass substrate using a RF magnetron sputter (Helix Technology, Hsinchu, Taiwan). The sputtering was conducted at a vacuum pressure of 6×10^{-4} Pa and room temperature for 5 min. High purity Ar with a constant flow rate of 3 cm^3/min was used. The microstructure of the as-deposited films was examined using a scanning electron microscope (SEM, LEO 1530). Electrical properties of the films

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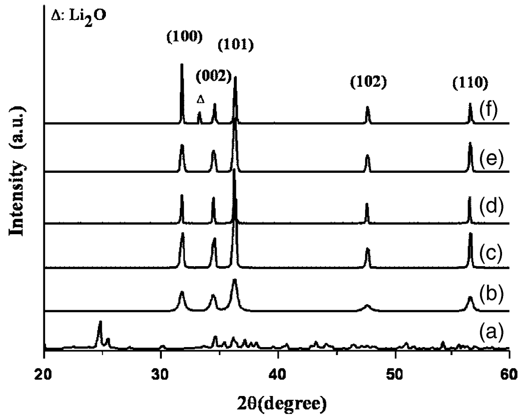

Fig. 1. X-ray diffraction patterns of the $Li_XZn_{1-X}O_{1-X/2}$ with $X = 0.002$ powders prepared by the soft-chemical-reaction method (a) as-dried and calcined at (b) 400°C, (c) 600°C, (d) 800°C, and (e) 1400°C, and the solid-state reaction method and calcined at (f) 1400°C for 2 h in air.

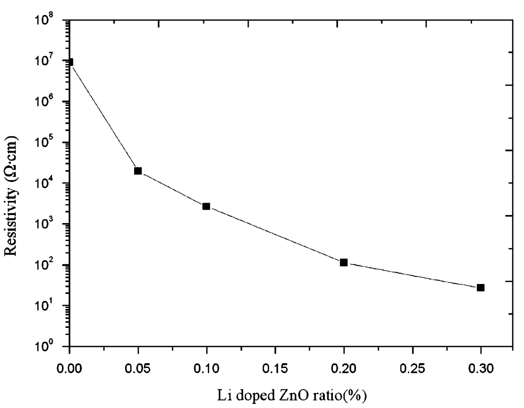

Fig. 2. Electrical resistivity of the $Li_XZn_{1-X}O_{1-X/2}$ compacts with different Li contents, densified at 1400°C for 2 h.

were measured at room temperature by an HL 5500PC Hall effect measurement system (Accent Optical Technologies, Milpitas, CA), which could measure electrical resistance $<10^{10}$ Ω, electrical mobility >0.01 cm^2/Vs, and carrier concentrations $>10^{12}$ cm^{-3} accurately. The electrical data measured for each experimental condition were consistent, and the average of three samples was reported. Optical properties of the films were characterized by measuring the transmittance (Spectrophotometer, Labguide, Taipei, Taiwan).

III. Results and Discussion

Figures 1(a)–(e) show typical XRD results of the $Li_XZn_{1-X}O_{1-X/2}$ with $X = 0.002$ powders prepared by the soft-chemical-reaction method and calcined at different temperatures for 2 h. It is found that the dry precursor gel complex forms a pure, crystalline ZnO phase at temperatures as low as 400°C, suggesting the incorporation of Li^+ into Zn^{+2} lattice to form a homogenous solid solution. Similar results are also observed for samples with different Li contents investigated. For the powders prepared by the solid-state reaction, however, two crystalline phases of Li_2O and ZnO are still found in the powder fired at 1400°C (Fig. 1(f)), indicating a poor mixing. The samples of $Li_XZn_{1-X}O_{1-X/2}$ with $X = 0$–0.003, which are prepared by the soft chemical reaction powder and fired at 1400°C for 2 h, exhibit >95% relative sintered density. Results of electrical resistivity for the sintered compacts with different Li contents are summarized in Fig. 2, where a significant drop in electrical resistivity with the presence of Li is noted, from 8.96×10^6 Ω·cm for pure ZnO to 1.96×10^4 Ω·cm for the sample with 0.05 mol% Li. The electrical resistivity continues decreasing with increasing Li content, to 2.7×10 Ω·cm for the sample with 0.3 mol% Li. As the ionic radius of Li^{+1} (0.059 nm)[11] is close to that of Zn^{+2} (0.060 nm),[11] it is believed that the above reduction trend in electrical resistivity is due to the incorporation of Li^{+1} onto the Zn^{+2} lattice, forming Li_{Zn}^{-1} acceptor and electronic hole (*h*) as follows: $Li_2O + 2V_{Zn} = 2Li_{Zn}^{-1} + O_O + 2h$, where Li_{Zn}^{-1} stands for a lithium atom on zinc site with one negative charge, O_o for a neutral oxygen atom on an oxygen site, *h* and for an electronic hole. More electronic holes are formed with an increasing Li concentration.[7]

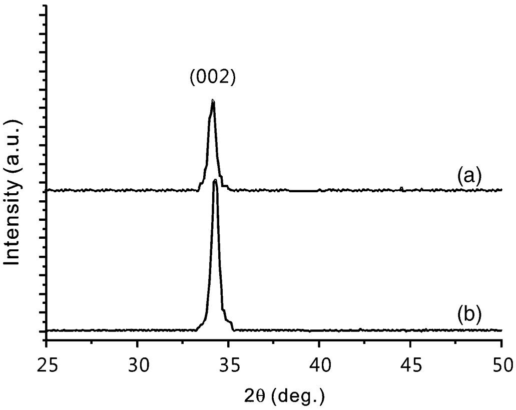

Fig. 3. X-ray diffraction patterns of the as-deposited ZnO films (a) with and (b) without 0.2 mol% Li, prepared by RF magetron sputtering method at room temperature.

Figure 3 shows XRD patterns of the as-deposited ZnO films with and without 0.2 mol% Li. The results clearly indicate that both films exhibit a highly preferred orientation of (002). Dense microstructure with uniform grains is found on the surface of the as-deposited films (Fig. 4(a)) with a thickness of ~500 nm (Fig. 4(b)). The electrical properties of $Li_XZn_{1-X}O_{1-X/2}$ films with and without 0.2 mol% Li are summarized in Table I. It is

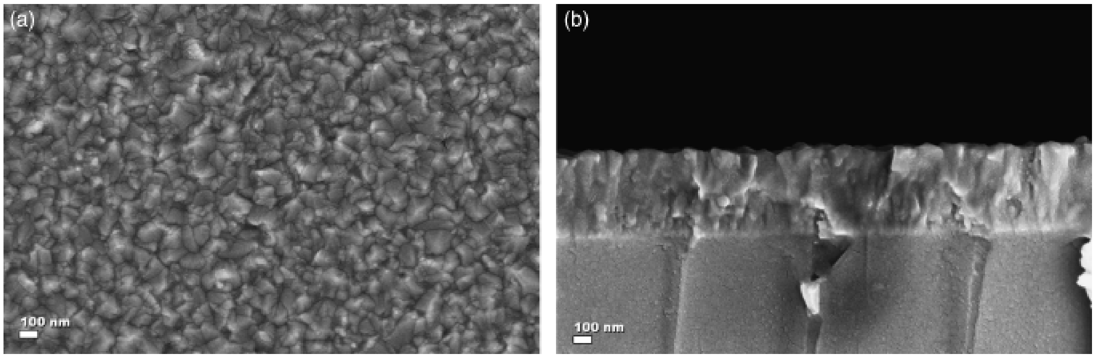

Fig. 4. Scanning electron microscopic microstructure of the as-deposited ZnO film doped with 0.2 mol% Li: (a) top and (b) fracture surfaces.

Table I. Electrical Properties of the as-Deposited ZnO Films with and without 0.2 mol% Li

	ZnO	ZnO Doped with 0.2 mol% Li
Resistivity (Ω-cm)	1.21×10^5	1.3
Mobility ($\mathrm{cm}^2 \cdot (\mathrm{V} \cdot \mathrm{s})^{-1}$)	0.36	0.77
Carrier concentration (cm^{-3})	1.43×10^{14}	6.67×10^{18}
Carrier type	n	p

found that the conduction of the pure ZnO film is *n*-type with an electrical resistivity of 1.21×10^5 $\Omega \cdot \mathrm{cm}$, Hall mobility of 0.36 $\mathrm{cm}^2 \cdot (\mathrm{V} \cdot \mathrm{s})^{-1}$, and a carrier concentration of 1.43×10^{14} cm^{-3}. In contrast, the Li-doped ZnO film exhibits *p*-type conduction with a much lower electrical resistivity of 1.3 $\Omega \cdot \mathrm{cm}$, larger Hall mobility of 0.77 $\mathrm{cm}^2 \cdot (\mathrm{V} \cdot \mathrm{s})^{-1}$ and higher carrier concentration of 6.67×10^{18} cm^{-3} than those of undoped ZnO film. Again, the above results are attributed to the presence of the Li acceptor, caused by the incorporation of Li^+ into the Zn^{+2} lattice resulting in the formation of oxygen vacancy. Data in Table I also indicate that both films have lower electrical resistivity than those of bulk samples (Fig. 2). This is due to the presence of grain boundary, i.e., polycrystalline structure without a preferred orientation observed in the bulk samples in relative to those of highly oriented films in (002). Figure 5 shows the optical transmittance of the as-deposited ZnO films with and without 0.2 mol% Li. A high transmittance of 80%–90% in the visible region, which is required for a transparent *p–n* junction, is observed. Moreover, the Li-doped ZnO film exhibits a higher optical transmittance than that of pure ZnO film.

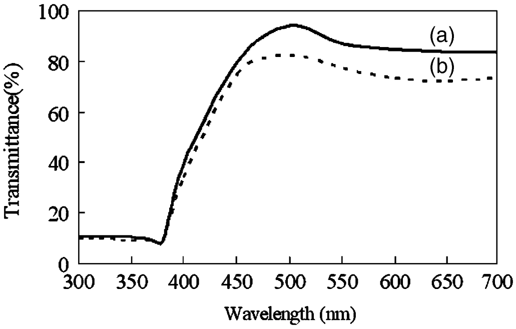

Fig. 5. Optical transmittance spectra of the as-deposited ZnO films doped (a) with and (b) without 0.2 mol% Li, fabricated by RF magnetron sputtering method at room temperature.

IV. Conclusions

A *p*-type Li-doped ZnO film is fabricated by the RF magnetron sputtering method at room temperature. The pure, crystalline sputtering target of $\mathrm{Li}_X\mathrm{Zn}_{1-X}\mathrm{O}_{1-X/2}$ with $X = 0$–0.3 mol% is prepared by the powder synthesized by a soft-chemical-reaction method. The powder can be densified at 1400°C, and the resulting compacts exhibit a decreasing trend of electrical resistivity, from 1.96×10^4 $\Omega \cdot \mathrm{cm}$ at 0.05 mol% Li to 2.78×10 $\Omega \cdot \mathrm{cm}$ at 0.3 mol% Li. The $\mathrm{Li}_X\mathrm{Zn}_{1-X}\mathrm{O}_{1-X/2}$ film with 0.2 mol% Li has a thickness of ~ 500 nm, which exhibits an electrical resistivity of 1.3 $\Omega \cdot \mathrm{cm}$ with a Hall mobility of 0.77 $\mathrm{cm}^2 \cdot (\mathrm{V} \cdot \mathrm{s})^{-1}$ and a carrier concentration of 6.67×10^{18} cm^{-3}, and a high optical transmittance of 90% in the visible region.

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