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Effect of energetic electron beam treatment on Ga-doped ZnO thin films

Solbaro Kim [a], Changheon Kim [a], Chaehwan Jeong [b], Sangwoo Lim [a,*]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea
[b] Applied Optics & Energy Research Group, Korea Institute of Industrial Technology, 1110-9 Oryong-dong, Buk-gu, Gwangju 500-480, Republic of Korea

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ABSTRACT

Transparent conductive zinc oxide (ZnO) thin films were synthesized by a sol–gel spin coating method with the addition of $Ga(NO_3)_3$ in a $Zn(CH_3COO)_2$ solution and exposed to electron beam treatment. The UV–Vis spectra demonstrated that all of the films had transmittances of over 85% in the visible region. When $Ga(NO_3)_3$ was added to the ZnO precursor solution, the resistivity of the ZnO thin film decreased and the carrier concentration increased significantly. After electron beam treatment was performed on the 0.4 at.% Ga-doped ZnO film, the optical band gap increased and the resistivity significantly decreased resulting from the increases of the carrier concentration and mobility. By combining Ga doping and electron beam treatment, the resistivity of the ZnO thin film was reduced by a factor of nine hundred.

1. Introduction

Indium tin oxide (ITO) has been widely studied and used as a transparent conductive oxide (TCO) [1–3]. However, ITO contains indium, which is a rare and toxic material. Therefore, zinc oxide (ZnO), which has a wide band gap energy (3.37 eV), large excitation binding energy (60 meV), and a high optical transmittance [4,5], is regarded as one of the substitutes for ITO. ZnO thin films have been used in various applications such as light emitting devices (LED), solar cells, thin film transistors (TFT), optoelectronic devices, and organic light emitting diodes (OLED) [6–10].

There are various techniques used to prepare ZnO thin films. For example, the available vacuum processes include chemical vapor deposition (CVD) [11], atomic layer deposition (ALD) [12], and radio-frequency (RF) magnetron sputtering [13]. When ZnO films are prepared by a vacuum process, they possess better electrical properties than those prepared by non-vacuum processes. For example, electrical resistivities as low as 1.1×10^{-2}–7.8×10^{-2} Ωcm [14–16], 4×10^{-3}–1.1×10^{-2} Ωcm [17–19], and 1.1×10^{-2}–4.5×10^{-2} Ωcm [20–22] have been obtained from CVD, ALD, and RF magnetron sputtering techniques, respectively. However, the main drawbacks of vacuum processes are their high production cost and low deposition rate. Therefore, it is attractive to synthesize transparent conductive ZnO thin films by a non-vacuum sol–gel method. Considering that the resistivity of ZnO films prepared by sol–gel methods is as high as on the order of 10^2 Ωcm [23–25], it is important for non-vacuum prepared ZnO films to possess electrical properties comparable to those prepared by vacuum processes [26].

The simplest method to improve the electrical properties of ZnO thin films is doping a dopant into ZnO. In general, group III elements such as Al, Ga, and In are doped into ZnO thin films, which produces free electrons by substituting trivalent ions for divalent Zn^{2+} ions, resulting in an increase of the carrier concentration and a decrease of resistivity [27–30]. However, it causes environmental issues because of its toxicity [31]. Doping of Al produces inferior electrical properties compared to In or Ga. According to a previous report from Gabás, the resistivity of Al-doped ZnO thin films is on the order of 10^{-2} Ωcm, while In or Ga-doped ZnO thin films possessed resistivities as low as on the order of 10^{-3} Ωcm [30,32]. In particular, Ga is a non-toxic material which shows prominent electrical properties [29,32]. On the other hand, ZnO films show improved crystalline and electrical properties when they are annealed at an elevated temperature [33,34]. For example, Sheu et al. reported that the crystallinity of Ga-doped ZnO films was improved and the resistivity was reduced from 8×10^{-3} to 6×10^{-4} Ωcm when the annealing temperature was increased from 400 to 700 °C [34]. However, the annealing process has a disadvantage in terms of the feasibility of the mass production process because the ramping up and cooling down of a furnace are time consuming tasks.

* Corresponding author. Tel.: +82 2 2123 5754; fax: +82 2 312 6401.
E-mail address: swlim@yonsei.ac.kr (S. Lim).

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Meanwhile, exposure of materials to electron beams is known to modify the crystallite size [35–38]. In particular, electron beam treatment can be operated at room temperature with a short process time, which can be an alternative to annealing sol–gel synthesized ZnO films. Therefore, in order to improve the electrical properties of ZnO thin films prepared by a sol–gel method, we adopted doping of Ga elements in ZnO films with energetic electron beam treatment in this study.

2. Experimental details

The precursor used to synthesize ZnO thin films was prepared by adding 0.5 M zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, ≥98%, Sigma–Aldrich) into 50 ml of 2-methoxyethanol ($CH_3O(CH_2)_2OH$, ≥99.3%, Sigma–Aldrich). Gallium(III) nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$, 99.9%, Sigma–Aldrich) was optionally added to the precursor solution. The concentration of the Ga dopant was varied among 0, 0.5, 1, and 2 mol% with respect to Zn. Then, 0.5 M monoethylamine ($NH_2(CH_2)_2OH$, ≥ 99.0%, Sigma–Aldrich) was added into the solution which was stirred at 60 °C for 3 h using a magnetic stirrer until a clear and homogeneous solution was obtained. ZnO thin films were prepared by spin coating on soda lime glass substrates (2.5 × 2.5 cm). First, the glass substrates were cleaned with acetone and isopropyl alcohol using an ultrasonic cleaner for 10 min. The spin coating process was conducted at a spin rate of 3000 rpm for 20 s at room temperature. The samples were dried on a hot plate at 300 °C for 5 min after each spin coating cycle to remove organic residue and solvent from the surface. The spin coating and drying cycles were repeated eight times to achieve a thickness of 150 nm and then, the samples were annealed in an Ar atmosphere furnace at 500 °C for 2 h.

The energetic electron beam treatment was implemented by applying coupled plasma ($\rho = 10^{11}$–10^{13} cm^{-3}) with an Ar flow rate of 7 sccm. The RF power and process time of the electron beam treatment were fixed at 300 W and 1 min, respectively, at 0.67 Pa. In order to control the electron dose and intensity of the electron beam irradiation, different beam energies of 2, 3, and 4 keV were applied. Electron beam treatment was conducted on the Ga-doped ZnO thin film (0.5 mol% Ga) which showed the lowest resistivity.

X-ray diffraction (Philips X'pert Pro X-ray diffractometer) with a Cu Kα radiation source (λ = 1.54056 Å) was used to analyze the crystal structure and orientation of the ZnO thin films. The results were used to obtain the average crystallite sizes of the ZnO films. X-ray photoelectron spectroscopy (K-alpha, Thermo U.K., monochromated) was used to investigate the chemical state and atomic concentration of each material in the ZnO thin films by using an Al Kα source. The optical transmittance of the ZnO films was measured by UV–visible spectroscopy (Varian, Cary-500) and the optical band gap energy of the ZnO films was evaluated using the transmittance data and Tauc's model. The electrical properties of the ZnO films were evaluated by Hall measurements (HMS 3000, Ecopia).

3. Results and discussion

Fig. 1(a) and (b) shows the XRD patterns of the differentially Ga-doped ZnO thin films and Ga-doped ZnO thin films subjected to different electron beam treatments. All of the films exhibited (002), (100), and (101) peaks and a strong (002) peak intensity, which reflect a wurtzite ZnO crystal structure. It is noted that the intensity of the (002) orientation peak significantly decreased with increasing Ga doping concentration, which implies the degradation

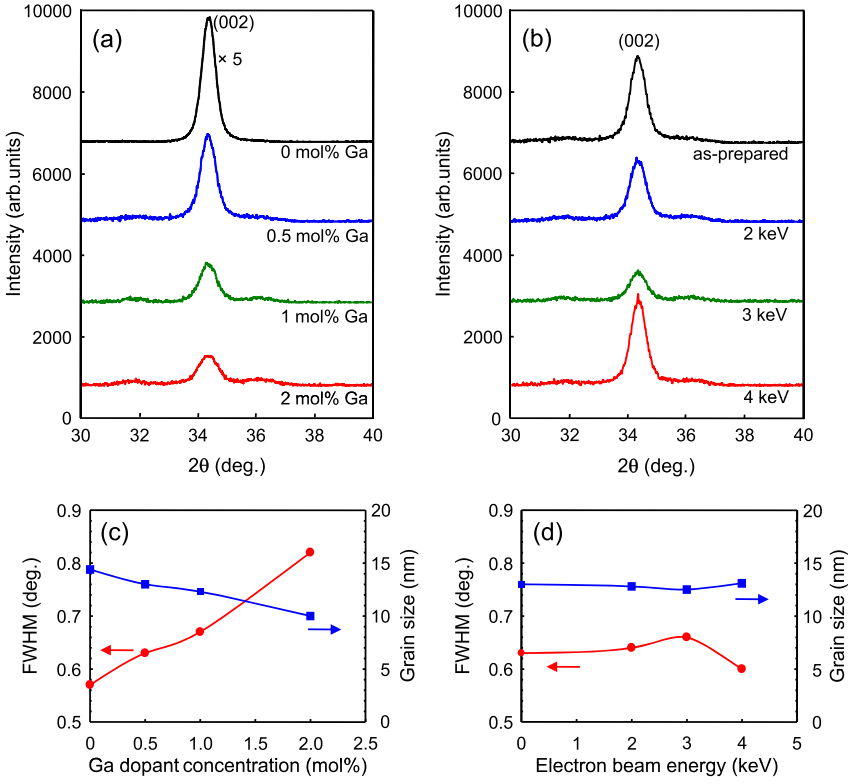

Fig. 1. XRD patterns of the (a) undoped and Ga-doped ZnO thin films, and (b) Ga-doped ZnO thin films prepared using 0.5 mol% Ga dopant after exposure to the electron beam. (c) The XRD FWHM and grain size obtained from Scherrer's formula for the (a) undoped and Ga-doped ZnO thin films, and (d) Ga-doped ZnO thin films prepared using 0.5 mol% Ga dopant after exposure to the electron beam.