Transparent Conducting Ga-doped ZnO Thin Film for Flat-Panel Displays with a Sol-gel Spin Coating

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Abstract

A novel non-alkoxide sol-gel process for synthesizing Ga-doped ZnO thin film on glass was derived for possible use as a transparent electrode in flat-panel displays, using zinc acetate dehydrate as the starting material. The structural and electrical properties of thin films have been characterized as functions of Ga addition and post-heat-treatments. Their carrier density, Hall mobility, and optical transmittance were measured and discussed herein to explain the characteristics of the sol-gel-derived Ga-doped ZnO thin film on glass.

Keywords : transparent conducting oxide, ZnO, thin film, sol-gel, glass substrate

Impurity-doped ZnO is an attractive transparent conducting oxide (TCO) for potential application as a transparent electrode in flat-panel displays (FPDs) and solar cells [1, 2]. ZnO is nontoxic, abundant, and inexpensive [3], and the electrical and optical properties of impurity-doped ZnO are comparable to those of the expensive indium tin oxide (ITO), which is currently being used commercially in liquid crystal displays (LCDs), plasma display panels (PDPs), and organic light-emitting displays (OLEDs) [3, 4]. Transparent conducting thin films require low electrical resistivity, high optical transmittance within the visible range, and high resistance to degradation under normal operating conditions [1-5].

This paper reports a novel non-alkoxide sol-gel process for depositing Ga-doped ZnO transparent conducting thin films on glass. The sol-gel process is considered an inexpensive, simple, and very flexible process for synthesizing large-area thin films of any material. The process allows the desired composition of the host material with controlled impurities and a high degree of uniformity.

In this study, zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was used as the starting material. An equal molar amount of 2-methoxyethanol and monoethanolamine (MEA) was used as the solvent. Zinc acetate dehydrate was dissolved in the solvent to a concentration of 0.75 M. Gallium acetylacetonate was used as the dopant precursor. The Ga composition was initially controlled at % of Ga and Zn. The final clear solution was aged for 48 hrs before the Ga-doped ZnO thin film was spin-coated onto an SiO_2-deposited (25 nm) soda lime glass substrate with a total thickness of 1.1 mm. Fig. 1 shows a flowchart of the procedure that was used for depositing the Ga-doped ZnO thin films using sol-gel spin coating. The first post-heat-treatment was performed in a tube furnace in air at 550℃, and the second was performed at 450℃ in a reducing atmosphere of 5% H_2–95% N_2.

X-ray diffraction (XRD, D8 Advanced X-ray, Bruker Axs.) was used to identify the crystalline phase and orientation of the growth surface of the sol-gel-derived Ga-doped ZnO thin film. Field emission scanning electron microscopy (FE-SEM S-4300, Hitachi) was used to observe the microstructure of the thin films. The electrical properties of the Ga-doped ZnO thin films were measured using a Hall effect measurement system (HMS-3000, Ecopia) operating at room temperature and employing the van der Pauw technique. The optical transmittance in the visible wavelength was measured using a UV-visible spectrophotometer (UV-3150, Shimazu).

Fig. 2 shows the XRD patterns of the sol-gel-coated ZnO:Ga thin film with different Ga doping concentrations. All the films showed crystallization of the sol-gel-coated ZnO thin films after post-heat-treatment at 550℃ and

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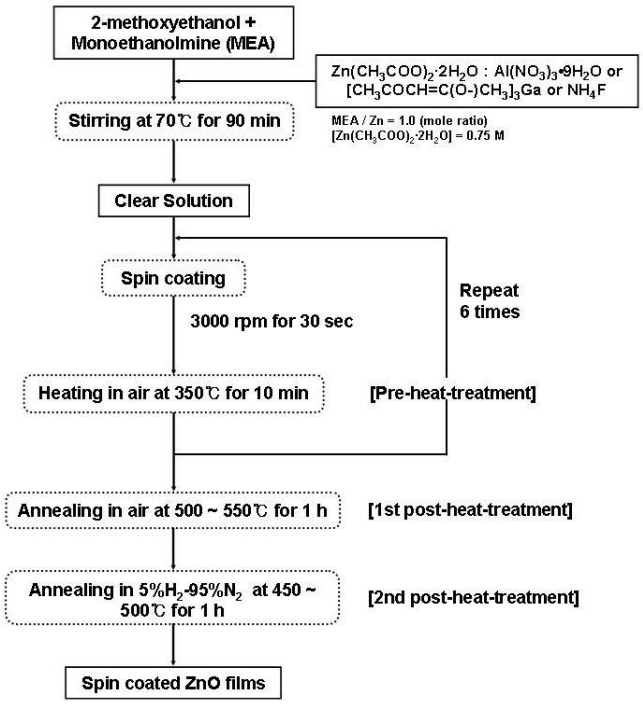

Fig. 1. Flowchart showing the sol-gel procedure for preparing the undoped ZnO and impurity-doped ZnO thin films.

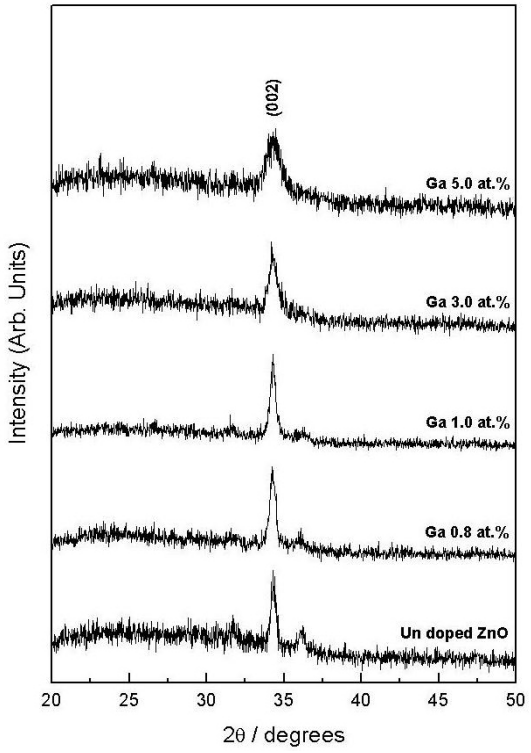

Fig. 2. XRD patterns of the sol-gel-derived Ga-doped ZnO thin films after the first post-heat-treatment in air at 550℃ for 1 hr and the second post-heat-treatment in 5% H_2-95% N_2 at 450℃ for 30 min.

450℃. All the samples (the undoped ZnO to the 5.0%-Ga-doped ZnO) showed a c-plane preferred orientation. In addition, the peak width broadened with increasing Ga, which suggests that the crystal size of the ZnO:Ga thin film decreases with an increasing Ga concentration.

Fig. 3 shows the FE-SEM images of the sol-gel-coated ZnO:Ga thin film with different Ga doping concentrations. The images show a nano-sized polycrystalline microstructure. Compared with the undoped ZnO sample, the grain size was significantly smaller in the films containing 0.25% Ga. The grain size decreased with an increasing Ga concentration, and the pores between the grains disappeared, showing an increasing film density with an increasing Ga concentration.

Fig. 4 shows the electrical resistivity of the Ga-doped ZnO thin film after the initial post-heat-treatment in air at 550℃, followed by a second post-heat-treatment at 450℃ in 5% H_2–95% N_2 as a function of the Ga dopant concentration. After the second post-heat-treatment in the reducing environment, the resistivity was approximately two orders of magnitude lower than that after the first post-heat- treat-

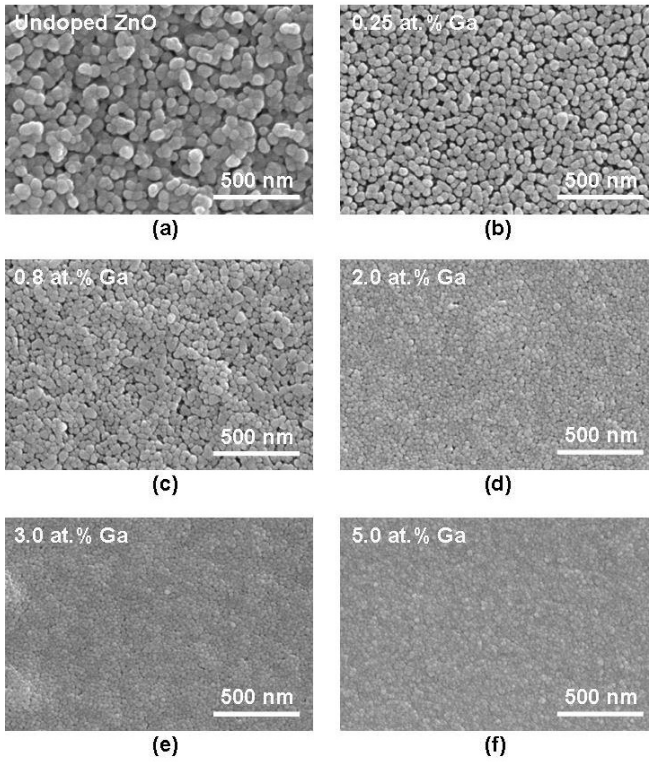

Fig. 3. Plan-view FE-SEM micrographs of the sol-gel-derived Ga-doped ZnO thin films after the first and second post-heat-treatments.

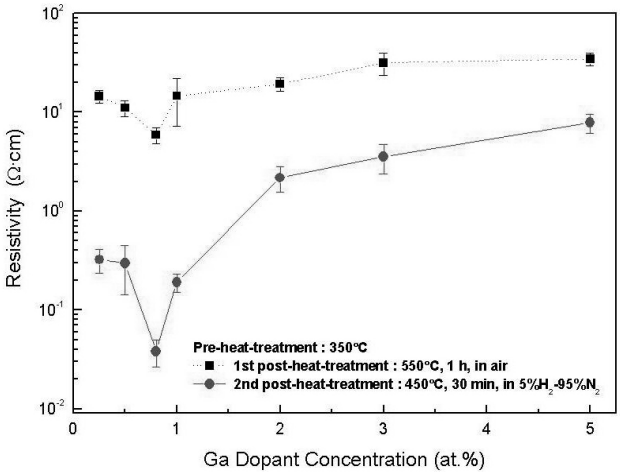

Fig. 4. Resistivity of the sol-gel-derived Ga-doped ZnO thin films as a function of the Ga impurity concentration after the first post-heat-treatment in air at 550℃ for 1 hr and the second post-heat-treatment in 5% H_2-95% N_2 at 450℃ for 30 min.

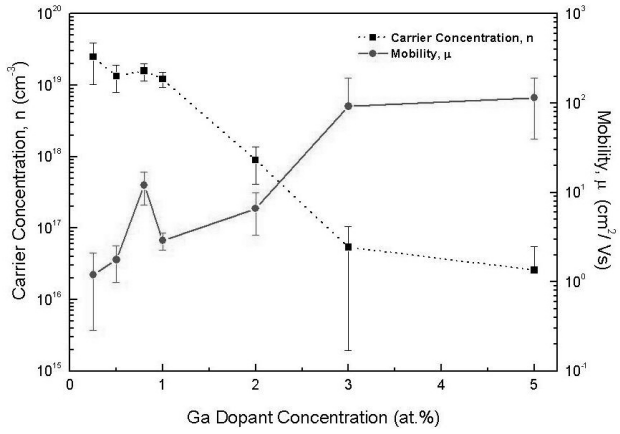

Fig. 5. Carrier concentration and Hall mobility of the sol-gel-derived Ga-doped ZnO thin film as a function of the Ga concentration after the first and second post-heat-treatments.

ment in air. Fig. 4 shows a minimum resistivity at 0.8% Ga after the first and the second post-heat-treatments. The minimum electrical resistivity of the Ga-doped ZnO thin film that was produced using this sol-gel process, after the second post-heat-treatment, was 2.32×10^{-2} Ωcm at 0.8% Ga. At higher Ga concentrations, the resistivity increased with an increasing Ga concentration.

Fig. 5 shows the carrier density and the Hall mobility as functions of the Ga dopant concentration. The negative sign of the Hall coefficient shows that the undoped ZnO- and Ga-doped ZnO thin films are both n-type, with electron charge carriers.

The highest carrier density was 4.1×10^{19} cm^{-3} in the film with 0.25% Ga. The carrier density decreased drastically at above 1% Ga to 10^{16} cm^{-3} at 5% Ga. This shows that the electrical activation of charge carriers (i.e., the ionization of Ga impurity atoms) becomes decreasingly efficient with an increasing Ga concentration in the sol-gel process.

The mobility did not decrease, however, with an increasing Ga concentration. The mobility showed an increasing tendency at 1-5% Ga, and was > 100 $cm^2V^{-1}s^{-1}$ at 5% Ga. Carrier-carrier scattering cannot be the dominant scattering mechanism because the active carrier density decreased drastically with an increasing Ga concentration of up to 10^{16} cm^{-3} at 5% Ga. The increase in mobility with a decreasing carrier concentration suggests that it is the ionized impurity scattering mechanism that is dominant and not the grain-boundary scattering mechanism because the grain size decreased with increasing Ga addition. As can be seen in the FWHMs of the XRD 002 diffraction peak in Fig. 1 and in the FE-SEM images in Fig. 2, the crystallized ZnO grains became smaller and the film became denser with an increasing Ga concentration, with fewer pores between the grains. In addition, the Hall measurements showed that the electron mobility increased with an increasing Ga concentration. Therefore, mobility is not a limiting factor that can explain the increasing tendency of electrical resistivity with an increasing Ga concentration. The electrically active carrier density decreased considerably, however, at above 1% Ga, which may have a much stronger effect on the increase in resistivity with increasing Ga addition.

Fig. 6 shows the transmittance spectra of the undoped

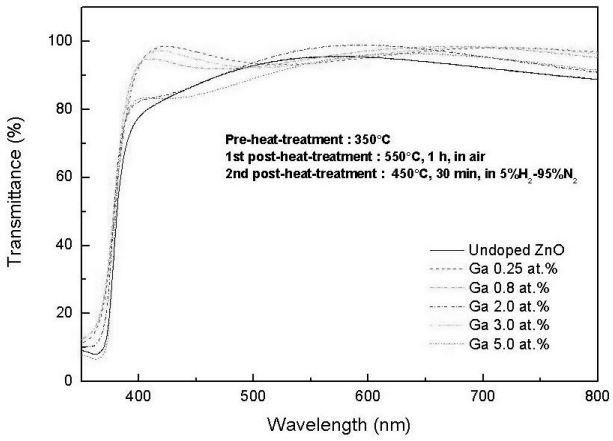

Fig. 6. Optical transmittance of the sol-gel-derived Ga-doped ZnO thin film after the first and second post-heat-treatments.

ZnO- and Ga-doped ZnO thin films produced using the sol-gel process. Within the visible range from 400 to 800 nm, the 300-nm-thick undoped ZnO thin film showed an average transmittance of approximately 92%. The thicknesses of the Ga-doped ZnO thin films were between 265 and 310 nm, and their average transmittance ranged from 94 to 97%. Overall, the optical transmittance of the Ga-doped thin film shows that the sol-gel-derived ZnO:Ga thin film has optical properties that make it suitable for use as a transparent electrode in flat-panel displays.

References

[1] T. Minami, MRS Bulletin, **25(8)**, 38 (2000)

[2] U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, and H. Morkoc, J.Appl. Phys., **98**, 041301 (2005)

[3] D.C. Plain, H.Y. Yeom, and B. Yaglioglu, in *Flexible Flat Panel Displays*, edited by G.P. Crawford (John Wiley & Sons, Singapore, 2005), p. 94.

[4] B.G. Lewis and D.C. Plain, MRS Bulletin, , **25(8)**, 22 (2000)

[5] D.S. Ginley and C. Bright, MRS Bulletin, , **25(8)**, 15 (2000)