

Al-doped ZnO via Sol-Gel Spin-coating as a Transparent Conducting Thin Film

Gil Mo Nam and Myoung Seok Kwon*

Abstract

A simple nonalkoxide sol-gel route for depositing an Al-doped ZnO thin film on a glass substrate was derived in this study. The initial Al dopant concentration in the sol-gel preparation varied and ranged from 0 to 5%. The sol-gel-derived thin films showed c-plane preferred crystallization of their hexagonal phase, with nanosized grain structures. First and second post-heat-treatments were carried out to improve the film's electrical resistivity. The carrier density and the Hall mobility were measured and discussed to explain the electrical resistivity. The optical transmittance within the visible range showed compatible properties, which indicates the possible use of Al-doped ZnO as a transparent electrode in flat panel displays.

Keywords : ZnO, TCO, Sol-Gel, Spin-coating, Al

1. Introduction

Impurity-doped ZnO is a candidate for 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 impurity-doped ZnO has electrical and optical properties that may be 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].

Unlike physical vapor deposition (e.g., sputtering and pulsed laser deposition) [1-5], which was used in the many previous TCO studies, 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 excellent compositional control with controlled do-

pants, a high degree of homogeneity on the molecular level, and a low crystallization temperature. In many of the previous sol-gel studies on the Al-doped ZnO, the dip-coating technique was used to make thin films on a glass substrate [6-10]. Recently, Kim and Tai reported a technique involving the sol-gel spin-coating of an Al-doped ZnO thin film on a glass substrate using isopropanol as the solvent and aluminum chloride hexahydrate as the dopant [11]. They reported the properties of the thin films as a function of heating temperature. These authors, on the other hand, reported a novel nonalkoxide sol-gel process for depositing a Ga-doped ZnO thin film on a glass substrate via spin-coating [12].

This study reports a simple nonalkoxide sol-gel route for depositing Al-doped ZnO transparent conducting thin films on a glass substrate, using 2-methoxyethanol and monoethanolamine (MEA) as solvents and aluminum nitrate as the dopant precursor. The structural, electrical, and optical properties of the spin-coated thin film were studied, with different Al dopant concentrations and post-heat-treatments.

2. Experiments

The novel sol-gel procedure for preparing the undoped and impurity-doped ZnO thin films that were used in this study was described in the authors' previous paper, with a flowchart [12]. Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was used as the starting material for ZnO [12]. Equal molar amounts of

Manuscript received November 25, 2008; Revised February 4, 2009; accepted for publication February 23, 2009.

This work was accomplished with support from the 2006 research fund of the University of Seoul.

* Member, KIDS

Corresponding Author: Myoung Seok Kwon

Department of Materials Science and Engineering, University of Seoul,
90 Jeonnon-dong, Dongdaemun-gu, Seoul 130-743, South Korea

E-mail: mskwon@uos.ac.kr Tel: 02-2210-5611 Fax: 02-2215-5863

2-methoxyethanol and monoethanolamine (MEA) were used as solvents [12]. Zinc acetate dehydrate was dissolved in the solvent to a concentration of 0.75 M [12]. Aluminum nitrate was used as the dopant precursor. The Al composition was controlled via the initial % of Al, defined by $100 [Al]/[Al+Zn]$. The resultant clear solution was aged at room temperature for 48 hr before the Al-doped ZnO thin film was spin-coated onto an SiO₂-deposited (25 nm) soda lime glass substrate with a total thickness of 1.1 mm. The spin-coating was done at room temperature, with a spinning rate of 3000 rpm, for 30 sec. After each coating, the film was preheated in air for 10 min, at 350°C. The spin-coating and preheating were repeated six times to achieve the desired total thickness. Finally, the first post-heat-treatment was performed in air at 530°C, and the second at 500°C, in a reducing atmosphere of 5% H₂ - 95% N₂.

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 Al-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 Al-doped ZnO thin films were measured using a Hall effect measurement system (HMS-3000, Ecopia) operated at room temperature, employing the Van der Pauw technique. The optical transmittance in the visible wavelength was measured using a UV-visible spectrophotometer (UV-3150, Shimadzu).

3. Results and Discussion

Fig. 1 shows the XRD patterns of the sol-gel-coated ZnO:Al thin film with different Al doping concentrations. All the films showed hexagonal-phase crystallization of the sol-gel-coated ZnO thin films after post-heat-treatment at 530 and 500°C (JCPDS card file no. 36-1451). All the samples (undoped to 5.0%-Al-doped ZnO) showed a c-plane preferred orientation. In addition, the peak width broadened with increasing Al concentration, which suggests that the crystallite size of the ZnO:Al thin film decreases with increasing Al concentration. The preferential orientation along the c-plane in the previous paper by Kim and Tai [11] was the same on the spin-coated Al-doped ZnO thin film, which employed isopropanol as the solvent and aluminum chloride hexahydrate as the dopant. The post-heating temperature was 500-650°C.

Fig. 2 shows the FE-SEM images of the sol-gel-coated

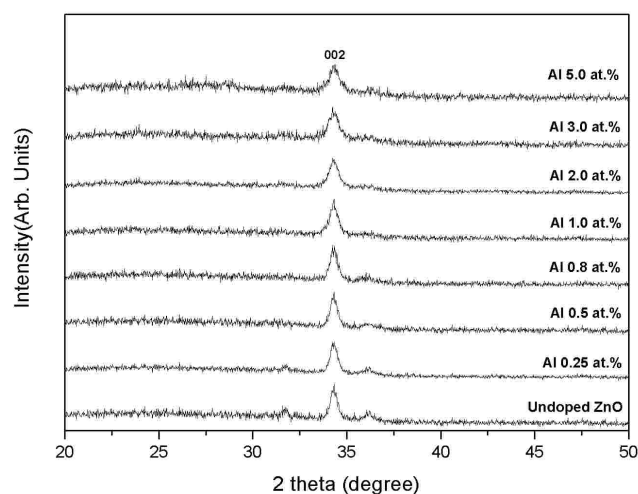


Fig. 1. XRD patterns of the sol-gel-derived Al-doped ZnO thin films after the first post-heat-treatment in air at 530°C for 1 hr, and after the second post-heat-treatment in 5% H₂ - 95% N₂ at 500°C for 30 min.

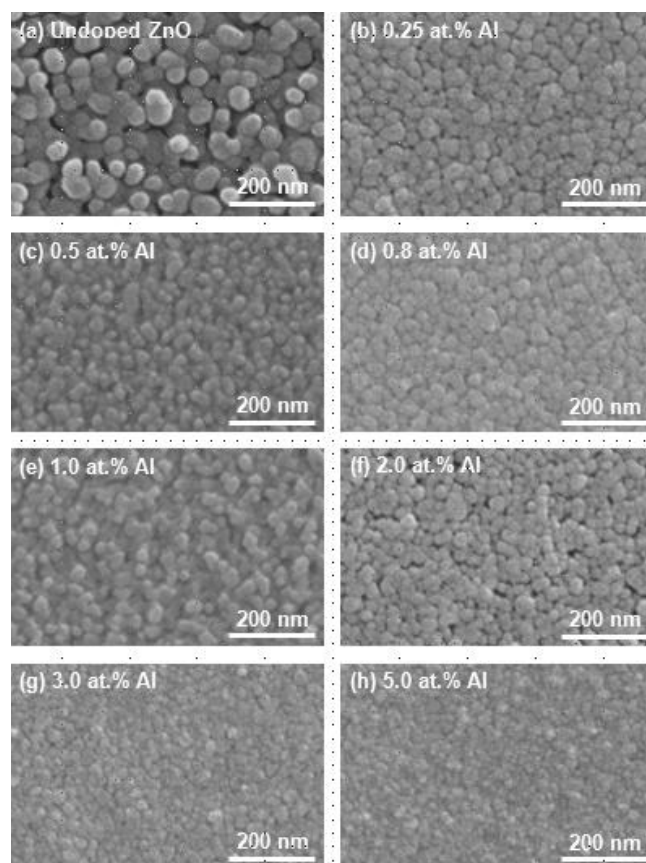


Fig. 2. Plain-view FE-SEM micrographs of the sol-gel-derived Al-doped ZnO thin films after the first and second post-heat-treatments.

ZnO:Al thin film with different Al doping concentrations. The images show nanosized polycrystalline microstructures. The undoped ZnO thin film showed many pores. Compared with the undoped ZnO thin film, the grain size was significantly smaller in the film containing 0.25% Al. The grain size decreased with increasing Al concentration, which could be predicted from the broadening of the XRD peak width in Fig. 1. The pores between the grains disappeared, as can be seen in Fig. 2, showing that the film became denser with increasing Al concentration.

Fig. 3 shows the electrical resistivity of the Al-doped ZnO thin film after the first post-heat-treatment in air at 530 °C, followed by the second post-heat-treatment at 500 °C in 5% H₂ - 95% N₂, as a function of the Al dopant concentration. After the first and second post-heat-treatments, the electrical resistivity of the film reached the minimum value at the specific Al concentration of 0.8%. Moreover, after the second post-heat-treatment in a reducing environment, the resistivity became approximately two orders of magnitude lower than that after the first post-heat-treatment in air. The minimum electrical resistivity of the Al-doped ZnO thin film derived through the sol-gel process was 0.28 Ωcm at 0.8% Al after the second post-heat-treatment. The electrical resistivity increased with increasing Al concentration.

Fig. 4 shows the carrier density and Hall mobility as functions of the Al dopant concentration. The negative sign of the Hall coefficient shows that all the undoped and Al-doped ZnO thin films are n-type, with electrons as charge

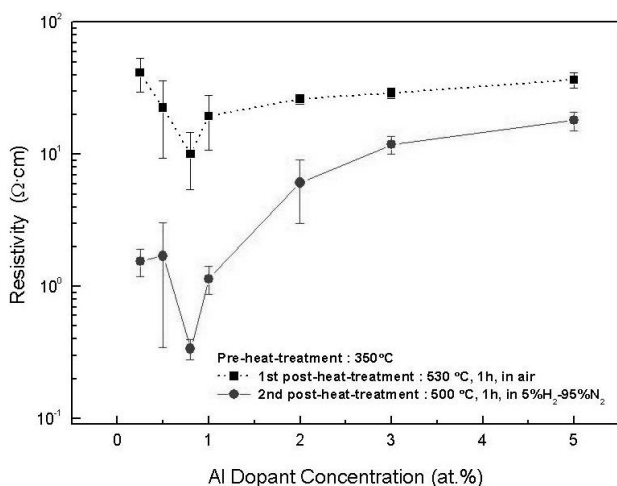


Fig. 3. Resistivity of the sol-gel-derived Al-doped ZnO thin films as a function of the Al impurity concentration after the first post-heat-treatment in air at 530 °C for 1 hr, and after the second post-heat-treatment in 5% H₂ - 95% N₂ at 500 °C for 30 min.

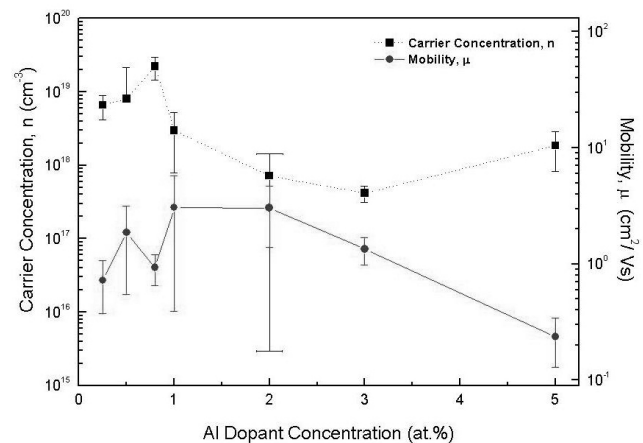


Fig. 4. Carrier concentration and Hall mobility of the sol-gel-derived Al-doped ZnO thin film as a function of the Al concentration after the first and second post-heat-treatments.

carriers.

The activated carrier density does not seem to be proportional to the Al dopant concentration. The carrier density reached its highest value of $3.37 \times 10^{19} \text{ cm}^{-3}$ in the film with 0.8% Al, and then decreased with higher Al concentrations. This shows that the electrical activation of the charge carriers (i.e., the ionization of the Al impurity atoms) becomes decreasingly efficient with increasing Al concentration in this sol-gel process.

The mobility in Fig. 4 showed an increasing tendency to reach the maximum value then a decreasing tendency above 2% Al. Carrier-carrier scattering cannot be the dominant scattering mechanism because the active carrier density decreased with increasing Al concentration. The decrease in mobility with increasing Al concentration suggests that it is the grain-boundary scattering mechanism rather than ionized impurity scattering that is dominant because the grain size decreased with Al addition. Based on the FWHMs of the XRD (002) diffraction peak in Fig. 1 and the FE-SEM images in Fig. 2, the sizes of the crystallized ZnO grains decreased and the film became denser with increasing Al concentration. The decreased mobility and carrier concentration can explain the tendency of the electrical resistivity to increase with increasing Al concentration above 1% Al. Unlike the reduced grain size, which was found to have a critical influence on mobility, the pores and density did not seem to have any critical influence within the experimental range.

The second post-heat-treatment in a reducing environ-

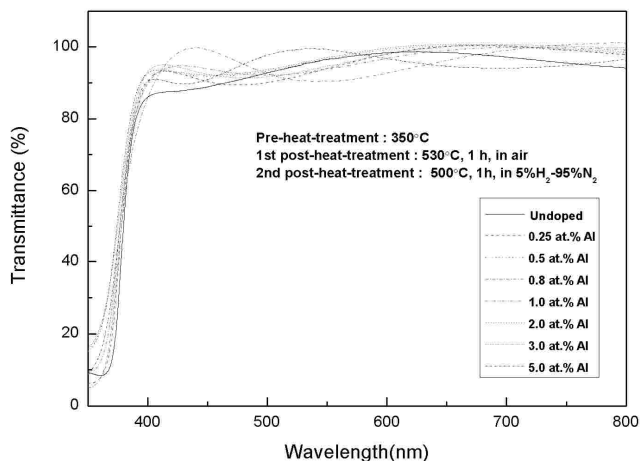


Fig. 5. Optical transmittance of the sol-gel-derived Al-doped ZnO thin film after the first and second post-heat-treatments.

ment efficiently reduced the electrical resistivity of the Al-doped ZnO thin film and affected mainly the oxygen vacancy concentration. The electron density could be increased, probably due to the increased donor concentration (i.e., oxygen vacancies), but the Al addition in the sol-gel process beyond the optimal Al concentration did not increase the carrier density. On the contrary, the carrier density decreased with Al addition, which may be due to the less efficient substitution of Al on the Zn site resulting from its solubility limit or from its related segregation as well as that of the Al complexes at the increased grain boundary regions.

Although the abrupt change in the resistivity and carrier concentration at 0.8% may be within the statistical-error margin, it can be concluded that the resistivity reached the minimum values of 1.0-2.0% in this study. Moreover, the carrier density showed a maximum value at around the same region of Al concentration, while the mobility decreased, although it was still above the maximum value. Therefore, the total resistivity can be expected to show a minimum value under a certain process window of Al concentration.

Fig. 5 shows the transmittance spectra of the undoped and Al-doped ZnO thin films derived through the sol-gel process. Within the visible range of 400-800 nm, the 300-nm-thick undoped ZnO thin film showed an average transmittance of approximately 94%. The Al-doped ZnO thin films were between 280 and 310 nm thick, and their average transmittance ranged from 95% to 97%. Overall, the optical transmittance of the Al-doped thin film shows that the sol-gel-derived ZnO:Al thin film has optical properties that make it suitable for use as a transparent electrode in flat panel displays.

4. Conclusions

The Al-doped ZnO thin film was derived through a novel nonalkoxide sol-gel spin-coating process on a glass substrate. All the films with an Al concentration of up to 5% showed a c-plane preferred orientation. The electrical resistivity showed the minimum value at a specific Al concentration. The second post-heat-treatment in a reducing environment reduced the electrical resistivity of the Al-doped ZnO thin film. The addition of Al dopant above the optimal Al concentration in the sol-gel process failed to raise the carrier density but reduced the mobility, probably due to the increased scattering from the grain boundaries resulting from the reduced grain sizes with higher Al concentrations.

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, Ltd, 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).
- [6] M. Ohyama, H. Kozuka, and T. Yoko, *J. Am. Ceram. Soc.* **81**, 1622 (1998).
- [7] T. Schuler and M.A. Aegerter, *Thin Solid Films* **351**, 125 (1999).
- [8] G.G. Valle, P. Hammer, S.H. Pulcinelli, and C.V. Santilli, *J. Eur. Cer. Soc.* **24**, 1009 (2004).
- [9] R. B. H. Tahar, *J. Eur. Cer. Soc.* **25**, 3301 (2005).
- [10] K.-M. Lin and P. Tsai, *Thin Solid Films* **515**, 8601 (2007).
- [11] Y.-S. Kim and W.-P. Tai, *Appl. Surf. Sci.* **253**, 4911 (2007).
- [12] G.M. Nam and M.S. Kwon, *J. Information Display* **9**, 8 (2008).