Journal of the Korean Crystal Growth and Crystal Technology
Vol. 18, No. 2 (2008) 72-75

Effect of heat-treatment on the structural and electrical properties of ZnO thin films by the sol-gel method

Seung-Yup Lee and Byung-Ok Park[†]

Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Korea

(Received January 10, 2008)
(Accepted March 21, 2008)

Abstract Zinc oxide (ZnO) thin films were prepared by a sol-gel method. The structural and electrical properties were investigated by varying drying and annealing temperatures. The thin films were coated (250 nm) by spin-coating method on glass substrates. The optimum drying temperature of ZnO thin films was 300°C where the resistivity was the lowest and the preferred c-axis orientation was the highest. The annealing was carried out in air and inert atmospheric conditions. The degree of the preferred c-axis orientation was estimated. The highest preferred c-axis orientation was recorded at 600°C. The preferred c-axis orientation and grain growth resulted in the mobility enhancement of the ZnO thin films, and the lowest resistivity was 0.62 Ω·cm at 600°C.

Key words Thin film, C-axis orientation, Zinc oxide, Sol-gel, Heat-treatment

1. Introduction

Zinc oxide (ZnO) is a n-type wide band gap semiconductor ($E_g = 3.3$ eV) and contains a hexagonal wurtzite crystalline structure. It has numerous advantages over other possible materials, including the following: its non-toxicity; good electrical, optical, and piezoelectric behavior; hydrogen plasma atmosphere stability; and its low price [1]. As a result of these positive properties, zinc oxide can be used in electronic and optoelectronic devices such as gas sensors [2], piezoelectric transducers [3], transparent electrodes in display [4], and photovoltaic devices [5].

ZnO thin films are usually prepared through a variety of thin film deposition techniques, including photo-atomic layer deposition [6], RF magnetron sputtering [7], chemical vapor deposition [8], spray pyrolysis [9], and sol-gel process [10]. The sol-gel technique offers many advantages such as highly homogeneity, large area coating, absence of vacuum, low cost, and high flexibility.

In the present study, ZnO thin films were prepared by the sol-gel method under varying drying and annealing temperatures. Thereby, heat-treatment effect on the structural and electrical properties of ZnO thin films was investigated.

2. Experimental

Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] was used as a starting material. 2-Methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The molar ratio of MEA to Zn ion maintained unity. The solution (0.75 M) was stirred at 40°C for 2 hours on a hot plate and aged for two days. As a result, a ZnO solution was completed for processing as ZnO thin films. The starting solution was dropped onto a substrate and rotated at 3000 rpm for 30 sec. A 15 × 15 × 1 mm bare glass (Corning Inc. 1737) was used as the substrate. The substrate was cleaned successively in an ultrasonic bath with acetone, ion exchanged water, and ethanol. After deposition through spin-coating, the thin films were dried at 250~500°C for 10 min on a hot plate. The coating to drying process was repeated until the desired thickness (250 nm) was obtained. The annealing process was conducted at 600°C only in air to investigate the optimum drying temperature. The annealing process was also conducted at varying air temperatures ranging from 400~700°C for 30 min and subsequently for 20 min under inert atmosphere conditions by directly inserting the films into a pre-heated electric tube furnace.

The structural properties of the films were analyzed by using an Philips X'pert APD X-ray diffractometer (XRD) with CuKα radiation at 40 kV, 30 mA. The surface morphology was observed with a Hitachi S-4200

[†] Corresponding author
Tel: +82-53-950-5634
Fax: +82-53-950-5645
E-mail: bopark@knu.ac.kr

scanning electron microscope (SEM) at 20 kV. The carrier concentration, mobility, and electrical resistivity of the thin films were determined by means of Hall measurements using a four-probe van-der-Paw technique.

3. Results and Discussion

Figure 1 shows the resistivity of ZnO thin films dried at 250~500°C and annealed only in air at 600°C. Whereas the annealing temperature was fixed, the drying temperatures were varied. At 250°C, the resistivity was relatively high (18.5 Ω·cm) but decreased sharply to 2.0 Ω·cm at 300°C. Subsequently, the resistivity increased in small increments, attaining a relatively high value of 12.5 Ω·cm at 500°C. Figure 2 illustrates XRD patterns of ZnO thin films dried at 250, 300, 400, and 500°C respectively, and annealed only in air at 600°C. While no sharp peaks were recorded at 250°C, a strong peak of (002) plane appeared at 300°C. Peak intensity of the (002) plane decreased and (100) & (101) peaks became stronger over 400°C. These results might be explained as follows: The solvent and stabilizer could not be removed at 250°C and prevented the thin films from being crystallized. Above 400°C, the drying temperatures were far higher than the boiling points of the solvent leading to abrupt solvent evaporation. Due to the abrupt evaporation process, atoms did not have enough time to attain to their stable positions. Thus, the resistivity increased with drying temperatures in the range of 400~500°C and the preferred c-axis orientation was not complete in the same temperature range. The lowest resistivity at 300°C was attributed to the high carrier mobility from the highly preferred c-axis orientation. The slow solvent evaporation allowed for a structural relaxation time period so that atoms could move to their favorable positions, thereby the preferred c-axis orientation was attained. Kim *et al.* [11] reported similar XRD patterns as shown in Fig. 2. However, these researchers used 2-propanol as a solvent in which the boiling point was noted at 82.5°C. Compared with 2-methoxyethanol (b.p.: 124°C) used in the present study, the difference between the respective boiling points was 41.5°C. The preferred c-axis orientation in that study therefore was noted 250°C.

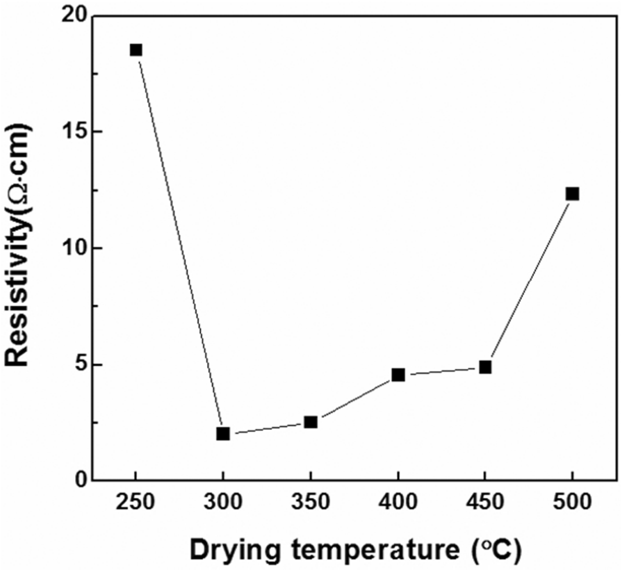

Fig. 1. Resistivity of ZnO thin films as a function of drying temperatures. (The dried thin films were annealed only in air at 600°C after the drying process).

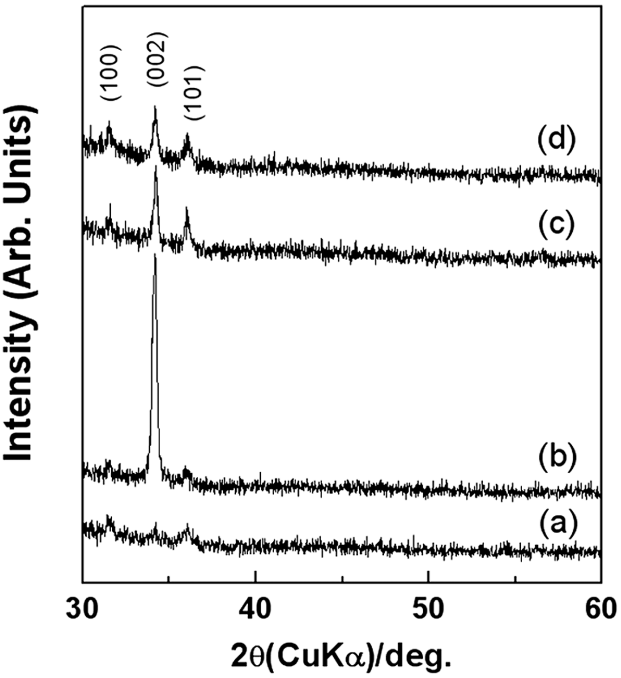

Fig. 2. XRD patterns of the films at several drying temperatures: (a) 250, (b) 300, (c) 400, and (d) 500°C. (All films were annealed only in air at stationary temperature of 600°C).

Based on Figs. 1 and 2, the optimum drying temperature was considered to be 300°C. Therefore, the thin films were dried at the stationary temperature (300°C), followed by annealing which was carried out at 400~700°C for 30 min in air and 20 min under inert atmospheric conditions. Figure 3 shows XRD patterns of the ZnO thin films as the annealing (in air and subsequently nitrogen gas) temperature increases. The peak of $2\theta = 34.2$ indicated the (002) plane, which could be easily identified with some published literatures [10, 12].

The (002) peak intensity increased along with the temperature and the strongest peak intensity was attatined at

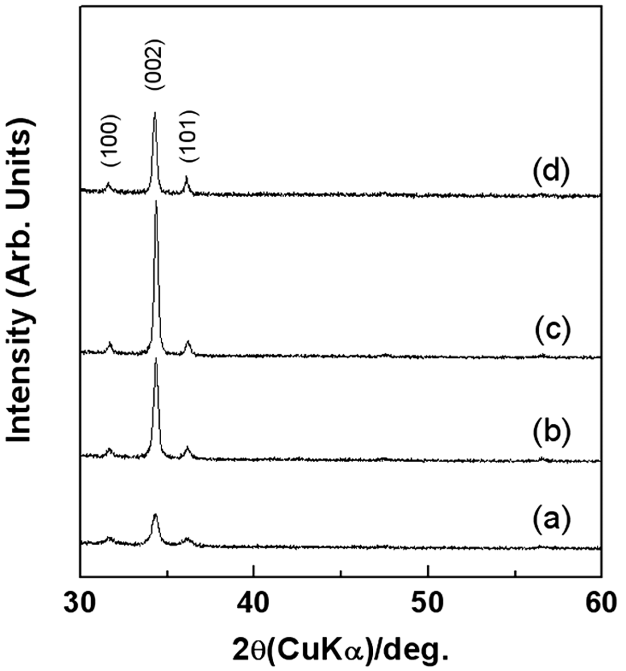

Fig. 3. XRD patterns of ZnO thin films as the annealing temperature varies: (a) 400, (b) 500, (c) 600, and (d) 700°C (The annealing process was conducted in air and subsequently nitrogen gas).

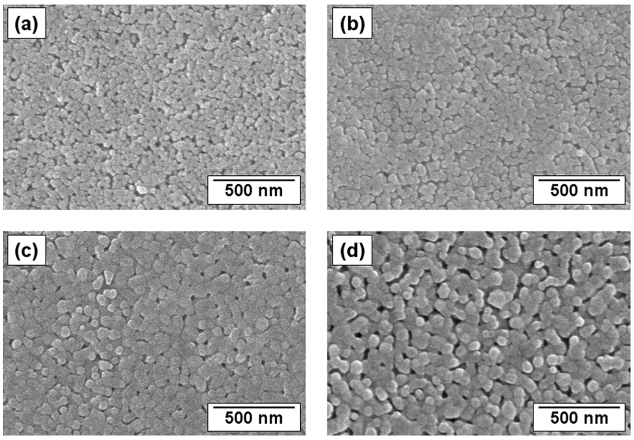

Fig. 4. Surface morphology of ZnO thin films at different annealing (in air and subsequently nitrogen gas) temperatures: (a) 400, (b) 500, (c) 600, and (d) 700°C.

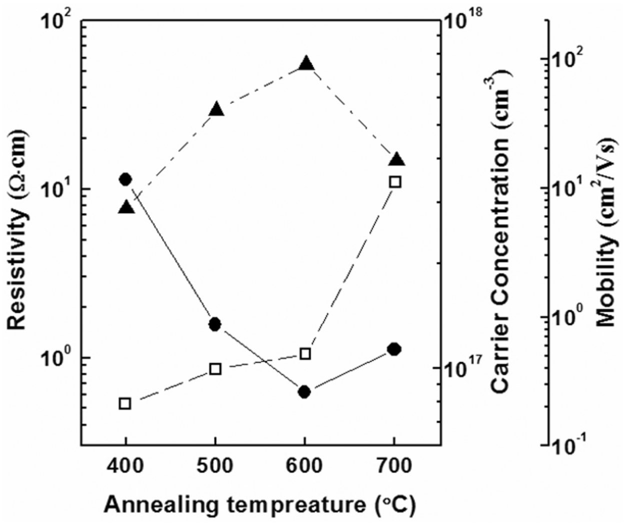

Fig. 5. Resistivity, carrier concentration, and mobility of ZnO films as a function of annealing (in air and subsequently nitrogen gas) temperature: ● resistivity, ☐ carrier concentration, and ▲ mobility.

600°C. However, at 700°C, the (002) peak intensity decreased and the preferred c-axis orientation also decreased. The degree of the preferred c-axis orientation was estimated by calculating $\alpha = I(002)/[I(002) + I(101)]$, where I(002) and I(101) were the peak intensities for the (002) plane and (101) plane, respectively. The values of α were 0.79, 0.89, 0.91, and 0.80 as the annealing temperature increased. The highest preferred c-axis orientation was therefore attained at 600°C.

SEM photographs of ZnO thin films with the corresponding annealing temperature are shown in Fig. 4. The annealing process was conducted in air and subsequently nitrogen gas. As the annealing temperature increased, the grain size of the ZnO films increased. Generally, the morphology of the thin films was porous. The surface pores disappeared with the rising temperature and films annealed at 600°C exhibited the lowest porosity and highest density. However, the pore size became larger at 700°C. Lee *et al.* [10] captured a SEM image that illustrated rough, porous, and agglomerated ZnO surface morphology through heat-treatment under nitrogen gas.

Figure 5 shows electrical properties of the ZnO thin films with corresponding increase of the annealing (in air and subsequently nitrogen gas) temperature. The mobility of the films increased with the annealing temperature and reached the maximum point at 600°C, and then decreased. Generally, mobility can be affected by grain boundary, ionized impurities, and phonons. With regard to polycrystalline thin films such as ZnO thin films, the grain boundary plays an important role in electron scattering, which decreases its mobility. Two factors affect electron scattering. The first is in regard to the c-axis orientation. The degree of the preferred c-axis orientation and mobility have a common feature in that the highest point was obtained at 600°C. The increase of thin films regularity causes the electrons to flow easily between the grains, and the c-axis orientation can be expected to decrease the electron scattering at the grain boundary. The second factor involved the grain size and porosity. The grain growth was observed with the increase of the annealing temperature as shown in Fig. 4. The increase of the grain size implied that the grain boundary scattering decreased. Moreover, both a decrease and increase of the porosity might affect its mobility. A decrease of the porosity could allow the electrons to move easily and the larger pores could prevent the electrons from moving in the thin films.

The carrier concentration increased with the annealing temperature. The increase from 400 to 600°C may be attributed to desorption of oxygen from grain boundaries during annealing under inert atmospheric conditions. The desorption of oxygen from heat-treated ZnO thin films is well-known [13]. The value at 700°C could not be explained by the desorption of oxygen because there was the huge increase at 700°C. Ogata *et al*. [14] attributed the increase in the carrier concentration with thermal annealing to the evaporation of oxygen. These researchers suggested that Zni and Vo formed by oxygen evaporation, acted as donors. The resistivity is proportional to the reciprocal product of carrier concentration and mobility. The resistivity of the films was the lowest (0.62 Ω·cm) at 600°C.

4. Conclusions

ZnO thin films were prepared by means of a sol-gel spin-coating method. The effect of the variations on the structural and electrical properties of ZnO thin films was investigated. It was determined that the optimal drying temperature is 300°C for the lowest resistivity of ZnO films. The XRD patterns showed that the degree of preferred c-axis orientation was the highest at 600°C. The surface morphology indicated that the ZnO thin films were porous and agglomerated and the lowest porosity was obtained at 600°C. The lowest resistivity of the ZnO thin films was 0.62 Ω·cm at 600°C.

References

[1] R.G. Gordon, "Criteria for choosing transparent conductors", MRS Bull. 25(8) (2000) 52.

[2] I. Stambolova, K. Konstantinov, S. Vassilev, P. Peshev and T. Tsacheva, "Lanthanum doped SnO_2 and ZnO thin films sensitive to ethanol and humidity", Mater. Chem. Phys. 63 (2000) 104.

[3] M. Benetti, D. Cannatá, F.D. Pietrantonio, E. Verona, P. Verardi, N. Scarisoreanu, D. Matei, G. Dinescu, A. Moldovan and M. Dinescu, "Structural and piezoelectric properties of pulsed laser deposited ZnO thin films", Superlattices Microstruct. 39 (2006) 366.

[4] M. Chen, Z.L. Pei, C. Sun, J. Gong, R.F. Huang and L.S. Wen, "ZAO: an attractive potential substitute for ITO in flat display panels", Mater. Sci. Eng. B 85 (2001) 212.

[5] T. Pauporté and D. Lincot, "Electrodeposition of Semi conductors foroptoelectronic devices: result on znic oxide", Electrochim. Acta 45 (2000) 3345.

[6] Y. Yamamoto, K. Saito, K. Takahashi and M. Konagai, "Preparation of boron-doped ZnO thin films by photoatomic layer deposition", Sol. Energ. Mater. Sol. Cells 65 (2001) 125.

[7] D. Song, P. Widenborg, W. Chin and A.G. Aberle, "Investigation of lateral parameter variations of Al-doped znic oxide films prepared on glass substrates by rf magnetron sputtering", Sol. Energ. Mater. Sol. Cells 73 (2002) 1.

[8] B.M. Ataev, A.M. Bagamadova, V.V. Mamedov, A.K. Omaev and M.R. Rabadanov, "Thermally stable, highly conductive, and transparent ZnO layers prepared in situ by chemical vapor deposition", J. Cryst. Growth 198/199 (1999) 1222.

[9] T.Y. Ma and S.C. Lee, "Effects of aluminum content and substrate temperature on the structural and electrical properties of aluminum-doped ZnO films prepared by ultrasonic spray pyrolysis", J. Mater. Sci. Mater. Electron. 11 (2000) 305.

[10] J.H. Lee, K.H. Ko and B.O. Park, "Electrical and optical properties of ZnO transparent conducting films by the sol-gel method", J. Cryst. Growth 247 (2003) 119.

[11] Y.S. Kim, W.P. Tai and S.J. Shu, "Effect of preheating temperature on structural and optical properties of ZnO thin films by sol-gel process", Thin Solid Films 491 (2005) 153.

[12] S. Fujihara, C. Sasaki and T. Kimura, "Crystallization behavior and origin of c-axis orientation in sol-gel-derived ZnO : Li thin films on glass substrates", Appl. Surf. Sci. 180 (2001) 341.

[13] S. Major, A. Banerjee and K.L. Chopra, "Annealing studies of undoped and indium-doped films of zinc oxide", Thin Solid Films 122 (1984) 31.

[14] K. Ogata, K. Sakurai, Sz. Fujita, Sg. Fujita and K. Matsushige, "Effects of thermal annealing of ZnO layers grown by MBE", J. Cryst. Growth 214-215 (2000) 312.