The Korean Journal of Ceramics, **3** [4] 249-252 (1997)

Preparation of Highly Oriented ZnO Thin Films Prepared by Sol-Gel Method

Cheol Jeong, Kyu-Seog Hwang, Jong-Ha Moon and Byung-Hoon Kim

Department of Ceramic Engineering, Chonnam National University,
300 Yongbongdong, Bukku, Kwangju 500-757, Korea
(Received September 26, 1997)

Highly oriented ZnO thin films were fabricated by dip-coating technique using zinc acetate - 2-methoxyethanol - 2-aminoethanol solution as starting materials, and effects of substrates on the film's orientation were investigated. Product films were obtained by prefiring at 300, 400, 500 and 550°C for 10 min, followed by final heat-treatment at the same temperatures as prefiring for 1 h. The *c*-axis oriented films on glass substrates were prepared by heat-treatment of prefiring films at 300-550°C, while films on alumina showed polycrystalline structure. Films with *c*-axis orientation exhibited lower specific resistivities than those of polycrystalline films with partial crack and pore.

Key words : Highly oriented ZnO thin film, Dip-coating technique, Polycrystalline structure, Specific resistivity

I. Introduction

ZnO is II-IV group compound semiconductor, having the wurtzite structure and cheap, abundant and stable materials. Because of their semiconducting, optoelectric, pyroelectric and transparent properties, it is used as varistor, transducer, sensor, infrared reflection films and transparent electrode etc,[1-7] and in particular those with preferential orientation along the *c*-axis have been demonstrated to work as surface acoustic wave (SAW) devices.[8]

In recent years, a number of physical and chemical methods, which include rf sputtering,[9] chemical vapor deposition (CVD)[10] and sol-gel method[11] have been employed to fabricate highly oriented ZnO thin films. Chemical solution process such as sol-gel method is a promising technique because of its low processing cost, ease of thickness control and large and complicated surface application. It is difficult, however, to obtain highly oriented films along the *c*-axis, although there have been several papers on the preparation of preferred oriented ZnO thin films by sol-gel method.[11,12]

In present work, we report the effect of the substrates on the orientation, specific resistivity and surface morphology of the product films.

II. Experimental procedure

A homogeneous coating solution was prepared by mixing of zinc acetate [$(CH_3COO)_2Zn \cdot 2H_2O$] and 2-methoxyethanol ($HOCH_2CH_2OCH_3$). Since zinc acetate has a low solubility in 2-methoxyethanol, 2-aminoethanol ($H_2HCH_2CH_2OH$) (MEA) was added to obtain clear solution (concentration: 0.6 mol zinc acetate/*l* 2-methoxyethanol) The molar ratio of MEA to zinc acetate was fixed at 1.0. The mixing solution was stirred for 2 h to obtain a homogeneous solution.

Gel films were prepared by dip-coating technique on successively cleaned slide glass and alumina plate at room temperature (withdrawal speed: 10 cm/min). The as-deposited films were immediately preheated at 300, 400, 500 and 550°C for 10 min, respectively, by directly inserting the samples into a preheated furnace. The dip-coating and preheating were repeated 15 times to adjust the thickness of the precursor films. After the final coating, precursor films were heat-treated at the same temperatures as prefiring for 1 h.

The thickness of ZnO films was about 1.2 μm confirmed by observation of the cross section of the fractured films with a scanning electron microscope (SEM; JEOL, JSM-5400). Crystallinity of the final films were analyzed by X-ray diffraction (XRD) θ-2θ scans using CuKα radiation. Specific resistivity of the films was measured by four probe method using silver paste as the upper electrode.

III. Results and Discussion

Fig. 1 shows XRD θ-2θ scans of ZnO thin films on slide glass heat-treated at various temperature. The (002) oriented ZnO thin films were obtained by final heat-treatment at 300°C and higher and the reflections of other phases were not recognized in these ZnO films, which means the films are highly oriented. Films heat-treated

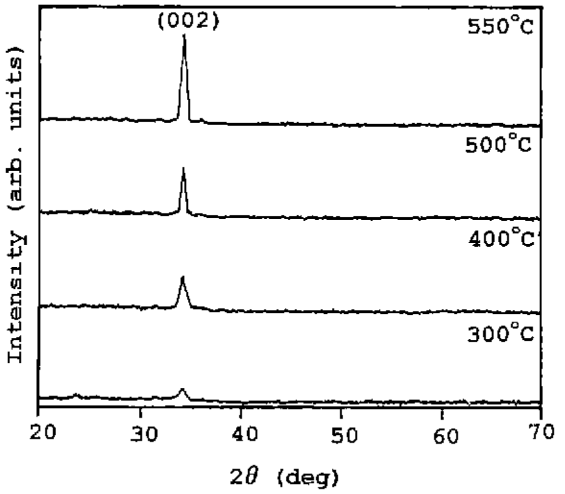


Fig. 1. XRD θ-2θ scans of ZnO films on slide glass substrates heat-treated at various temperature.

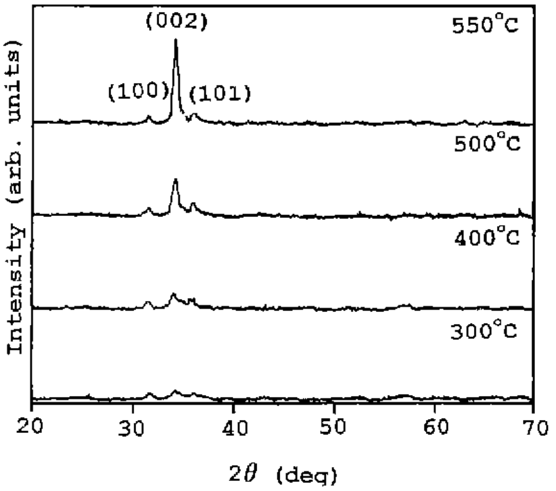


Fig. 2. XRD θ-2θ scans of ZnO films on alumina substrates heat-treated at various temperature.

at the higher temperature gave the stronger ZnO peaks.

Recently, a variety of slightly *c*-axis oriented ZnO films have been prepared by the sol-gel method using zinc acetate and iso-propanol as the starting materials.[13,14] It is difficult, however, to obtain preferred orientation of the films because other mis-oriented peaks such as (101) or (100) were easily recognized. On the contrary, in the present work, films strongly oriented along the *c*-axis can be prepared from 2-methoxyethanol and MEA as a solvent and an additive, respectively These can be explained by structural relaxation of the films as a function of vaporization rate of the solvents. Since the boiling points of 2-methoxyethanol and MEA are 125° and 170°C, respectively, the structural relaxation of the present film, which is induced by the lower vaporization rate of the solvent, resulting in dense precursor films and preferred crystal orientation On the other hand, in the case of water and iso-propanol with lower boiling points, unidirectional crystal growth may be suppressed by abrupt vaporization of the solvents during preheating, resulting in the lower orientation.[12]

Nextly, in order to investigate the effect of substrate structure on crystal growth, we prepared ZnO films on polycrystalline alumina substrates. Fig. 2 shows XRD θ-2θ scans of ZnO films on alumina substrates heat-treatment at various temperature. As clearly seen, evidence of mis-oriented peaks such as (101) and (100) was observed, while preferential orientation along the *c*-axis was observed for ZnO films on non-crystalline slide glass substrates. Ohyama *et al.*[12] reported that, in thinner film (<100 nm), the glass substrate probably disturbs the oriented crystal growth because of the random atomic arrangement of the substrate. On the other hand, the oriented grain growth in thicker film (multi-layered film) may easily occur because of the presence of slightly oriented grains in bottom layer. Thus, *c*-axis orientation of the present films on glass substrate may be attributed to film thickness.

Conclusively speaking, there are three possible effects on preferred orientation in present films on glass substrates. Firstly, ZnO oriented grain growth take place inherently, secondly, the lower vaporization rate of the solvent caues dense precursor films and preferred orientation. Finally, the film thickness may be sufficient to occur highly orientation. In the case of films on alumina substrates, on the otherhand, it is difficult to obtain oriented films. We assumed that polycrystalline substrate causes mis-oriented phases in ZnO films.

Further, to investigate the electrical property of these films, specific resistivity in the room temperature was measured. As seen in Fig. 3, in the case of preferred oriented films on slide glass substrate, the specific resistivity exists lower than that of polycrystalline films on alumina substrate.

To elucidate the effect of the surface morphology of the films on the specific resistivity, SEM observation was

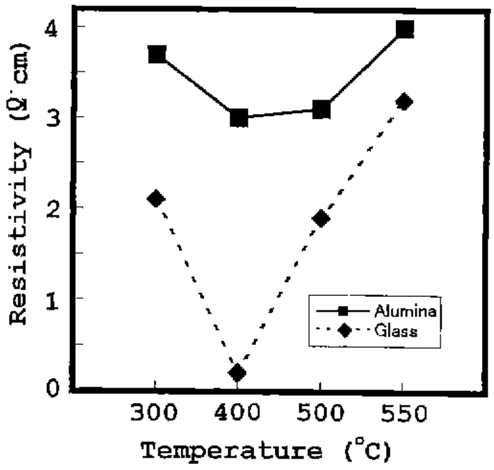
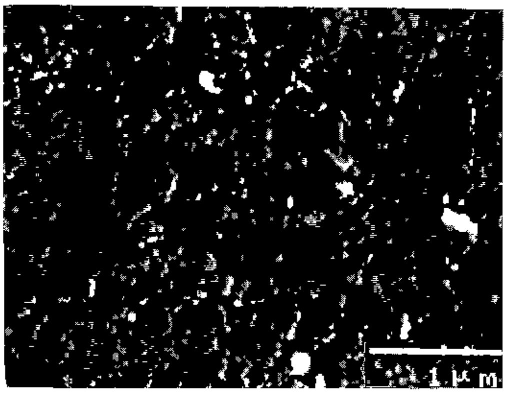


Fig. 3. Resistivity of ZnO films as a function of various heat-treatment temperature

performed for each of the substrates, and some differences were recognized among these films. Fig. 4 shows SEM photographs of the free surfaces for films on glass substrate (a) and alumina substrate (b) and the fractured cross section for films on glass substrate (c). When comparing these two films, an apparent large pore and micro-cracks were clearly recognized in films on alumina substrate as shown in Fig. 4 (b). This may be attributed to an effect of porous surface structure of alumina substrates, resulting in higher specific resistivity than that of films on glass substrates. Fractured surface of films was uniform and dense along the cross section direction (film thickness = 1.2 μm), in Fig. 4 (c). It should be emphasized that highly oriented films on amorphous substrates were successfully prepared by the simple and low-cost preparation procedure such as chemical solution process.

a) ZnO/Slide glass



b) ZnO/Alumina

c) ZnO/Slide glass

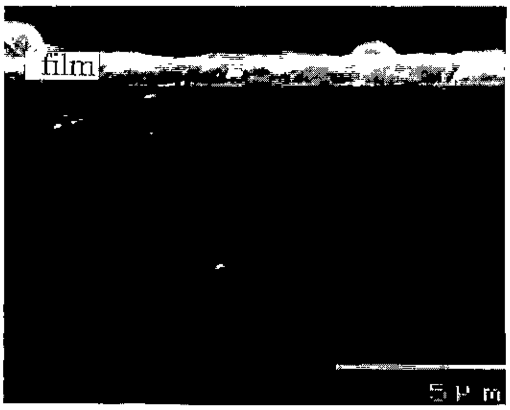


Fig. 4. SEM photographs of the free surfaces of films heated at 500°C on slide glass (a) and alumina (b) and fractured cross section of films on slide glass (c).

Further investigation is in progress to investigate the effects of substrates such as metal and lattice-matched crystal, to obtain highly oriented ZnO films with very smooth surface.

IV. Conclusion

Highly oriented ZnO thin films were fabricated by dip-coating technique using zinc acetate - 2-methoxyethanol - MEA solution as starting materials, and effects of substrates on the film's orientation were investigated. Product films were obtained by prefiring at 300, 400, 500 and 550°C for 10 min, followed by final heat-treatment at the same temperatures as prefiring for 1 h. The c-axis oriented films on glass substrates were prepared by heat-treatment of prefiring films at 300-550°C, while films on alumina showed polycrystalline structure. Films with c-axis orientation exhibited lower specific resistivities than those of polycrystalline films with partial crack and pore.

Acknowledgment

This work was supported by the Ministry of Education Research Fund (Advanced Materials) in 1995 and Fund of Automobile Research Center in Chonnam National University (1995).

References

1. T. K. Gupta, "Application of Zinc Oxide Varistors", *J. Am. Ceram. Soc*, **73**, 1817-1840 (1990).
2. M. N. Rahaman, L. C De Jonghe, J. A. Voigt and B. A. Tuttle, "Low-Temperature Sintering of Zinc Oxide Varistors", *J. Mater. Sci.*, **25**, 737-742 (1990).
3. D. F K Hennings, R Hartung and P J. L. Reijnen, "Grain Size Control in Low-Voltage Varistors", *J. Am. Ceram. Soc.*, **73**, 645-648 (1990)
4. F. C. M. Van De Pol, "Thin Film ZnO- Properties and Applications", *Ceramic Bull.*, **69**, 1959-1965 (1990).
5 W. H. G. Horsthuis, "ZnO Processing for Integrated Optic Sensors", *Thin Solid Films*, **137, 185-192 (1986).**
6. T. L. Tansley and D. F. Neeley, "Adsorption, Desorption and Conductivity of Sputtered Zinc Oxide Thin Films", *Thin Solid Films*, **121**, 95-107 (1984).
7. S. Matsushima, K. Abe, K. Kobayashi and G. Okada, "Oxygen-Sensing Properties of Sputtered ZnO Film Deposited on Sapphire under Ultra-Violet Illumination", *J. Mater. Sci. Lett.*, **11**, 1389-1391 (1992).
8. T. Mitsuyu, S. Ono and K. Wasa, "Structures and SAW

Propertied of rf-Sputtered Single-Crystal Films of ZnO on Sapphire", *J. Appl. Phys*, **51**, 2464-2470 (1980).

9. Z. C. Jin, I. Hamberg and C. G. Granqvist, "Optical Properties of Sputter-Deposited ZnO Al Thin Films", *J. Appl. Phys.*, **64**, 5117-5131 (1988).
10. T. Maruyama and J. Shionoya, "Zinc Oxide Thin Films Prepared by Chemical Vapor Deposition from Zinc Acetate", *J. Mater. Sci. Lett*, **11**, 170-172 (1992).
11. M. Ohyama, H. Kozuka, T. Yoko and S. Sakka, "Preparation of ZnO Films with Preperential Orientation by Sol-Gel Method", *J Ceram. Soc. Jpn.*, **104**, 296-300 (1996).
12. M. Ohyama, H. Kozuka and T. Yoko, "Sol-Gel Preparation of ZnO Films with Extremely Preferred Orientation along (002) Plane from Zinc Acetate Solution", *Thin Solid Films*, **306**, 78-85 (1997)
13. Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoura and Y. Ohya, "Photoconductivity of Ultrathin Zinc Oxide Films", *Jpn J Appl. Phys., Pt. 1*, **33**, 6611-6615 (1994).
14. S. Major, A. Banerjee and K. L. Chopra, "Highly Transparent and Conducting Indium-Doped Zinc Oxide Films by Spary Pyrolysis", *Thin Solid Films*, **108**, 333-340 (1983).