Journal of Ceramic Processing Research. Vol. 9, No. 6, pp. 638~642 (2008)

J O U R N A L O F
Ceramic Processing Research

Study of Ga-Doped ZnO films deposited on PET substrates by DC magnetron sputtering

D.Y. Lee[a], J.R. Lee[a], D.G. Kim[b], G.H. Lee[b] and P.K. Song[a,*]

[a]*Department of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea*
[b]*Surface Technology Research Center, Korea Institute of Materials Science (KIMS), 66, Sangnam-dong, Changwon-si, Gyeongnam, 641-010, Korea*

In this study, Ga-doped ZnO (GZO) films were deposited on unheated polyethylene terephthalate (PET) substrates by DC magnetron sputtering. The dependence of the structural, electrical and mechanical properties and surface morphology of the GZO films on their deposition conditions was investigated. The GZO films deposited at a sputtering power of 70 W and a P_{tot} of 2.0 Pa showed relatively good electrical, structural and optical properties and surface morphology. These results could be explained by the enhancement of the migration of the sputtered atoms (Zn, Ga, O) and low bombardment of the high energy particles (Ar^o, O^-). Therefore, the mechanical durability of the GZO films was related to their electrical and structural properties and surface morphology.

Key words: GZO, cyclic bending test, PET, DC magnetron sputtering, mechanical property.

Introduction

Transparent conducting oxide (TCO) films, which are degenerate wide band-gap semiconductors with a low resistivity and high transmittance in the visible light region, can be used for a wide range of highly useful applications, such as transparent electrodes in optoelectronic devices, flat panel displays (FPDs), and solar cells. Among the various TCO materials, indium tin oxide (ITO) films are generally used in these applications, because of their low resistivity and high transmittance. Recently, however, it was reported that Al- or Ga- doped zinc oxide films might replace ITO films as the TCO material of choice, due to their low cost, abundant raw material supply, non-toxicity, and excellent stability in a hydrogen plasma compared to ITO films [1-4]. Moreover, TCO films deposited on a polymer substrate have many merits, such as their low cost and lightweight, flexible and unbreakable properties, compared with those on a glass substrate. Therefore, they can be used in flexible displays, touch sensitive overlays, unbreakable heat reflecting mirrors, smart cards, electronic maps, etc. [5, 6]. There is a significant problem involved in depositing TCO films on polymer substrates, however, in that the substrate temperature should be relatively low, because polymer substrates have poor thermal stability. While ITO films deposited on polymer substrates have been extensively studied, ZnO films deposited on polymer substrates have not. Above all, no research into the mechanical durability of ZnO films under conditions of mechanical dynamic stress has been reported.

In this study, Ga-doped ZnO (GZO) films were deposited on polyethylene terephthalate (PET) substrates using DC magnetron sputtering at room temperature (RT). The dependence of the structural, electrical and mechanical properties and surface morphology of the GZO films on their deposition conditions was investigated.

*Corresponding author:
Tel : +82-51-510-2390
Fax: +82-51-512-0528
E-mail: pksong@pusan.ac.kr

Experimental Details

GZO films with thicknesses of 150-160 nm were deposited on hard coated PET (188 μm, 50 × 50 mm size, Omega-Whayeon Co., LTD) substrates using DC magnetron sputtering without substrate heating. The composition

Table 1. The deposition conditions for the GZO films.

Deposition	
Parameters	Conditions
Target	GZO (Ga_2O_3: 6.65 wt% ZnO : 93.35 wt%)
Substrate	Polyethylene Terephthalate (PET)
Base Pressure	~ 1×10^{-3} Pa
DC Sputtering Power	30-100 W
Total Gas Pressure	1.0-3.0 Pa
Target-Substrate Distance	50 mm
Sputtering Gas	Ar (60 sccm)
Substrate Temperature	RT
Film Thickness	150-160 nm

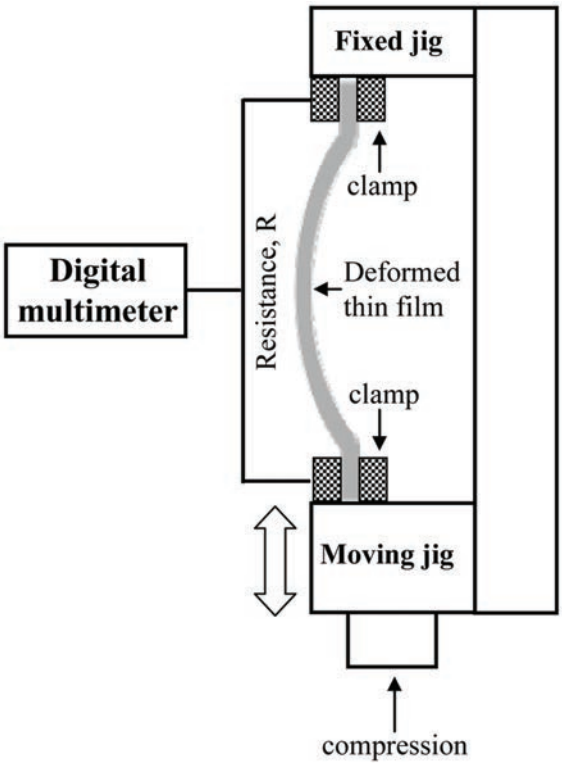

Fig. 1. Schematic diagram of the dynamic bending test system.

of the high density GZO target (Samsung Corning Co., LTD) was 93.35 wt% ZnO and 6.65 wt% Ga_2O_3. Deposition was carried out under various conditions, viz. a sputtering power in the range of 30-100 W and a total gas pressure in the range of 1.0-3.0 Pa. The detailed experimental parameters are given in Table 1. The GZO target was pre-sputtered for 5 minutes before the deposition, in order to eliminate the oxide layers from the target surface and thus ensure a high reproducibility of the films.

The thickness and deposition rate of the films were determined by a surface profiler (Dektak3, VEECO). The resistivity, carrier density, and Hall mobility at RT were measured by a four-point probe and Hall effect measurements (HMS-3000, ECOPIA). The microstructure and surface morphology of the films were studied by X-ray diffraction (XRD, Rigaku RINT 2000 series) and atomic force microscopy (AFM, XE-120, PSIA), respectively. The optical transmittance was measured using a UV-Visible spectrophotometer (HP 8453, Agilent) in the wavelength range from 200 to 1200 nm. Also, the mechanical durability of the films deposited on the PET substrates was monitored by a cyclic bending tester, as shown in Fig. 1. The cyclic bending test was carried out using a homemade fatigue machine at a total frequency of 0.08 Hz for 360 cycles (nearly 70 minutes), while maintaining a constant linear vertical movement with a 20 mm stroke. During the cyclic bending test, the change in electrical resistance (ΔR) of the films was continuously measured by a computer system with an Agilent 34401 A6 1/20 digital multimeter.

Results and Discussion

Figure 2 shows the change in resistance ($\Delta R/R_0$) in a dynamic stress mode for the GZO films deposited on the PET substrate under various conditions, where R_0 and ΔR represent the initial resistance and the difference between the initial and final resistance, respectively. Figs. 2(a)-2(d) show the $\Delta R/R_0$ values of the GZO films deposited at a sputtering power in the range of 30-100 W under a constant P_{tot} of 2.0 Pa. The $\Delta R/R_0$ value reached a minimum for the GZO film deposited at a sputtering power of 50 W and increased at lower or higher sputtering powers. The

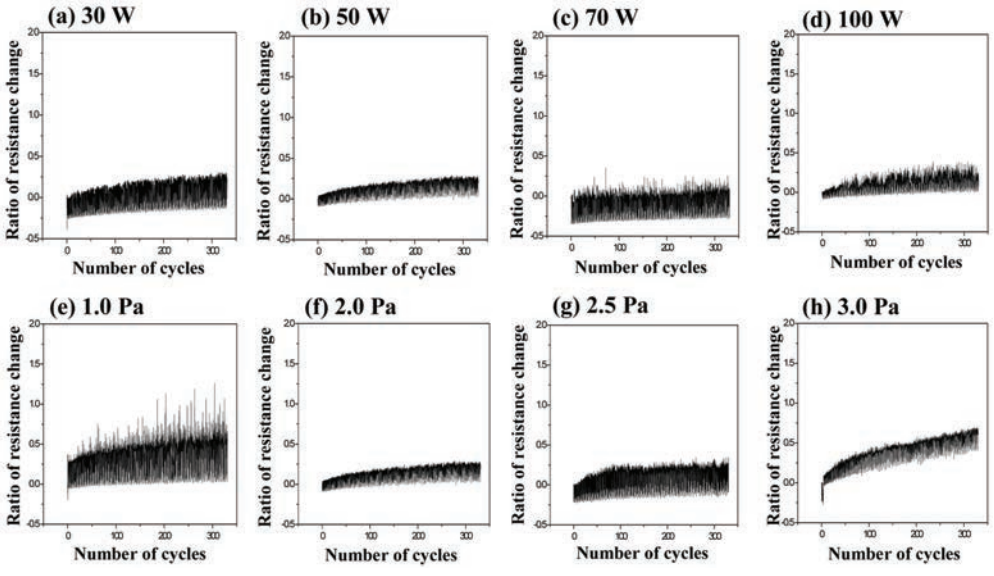

Fig. 2. Change in resistance ($\Delta R/R_0$) in a dynamic stress mode for the GZO films deposited on the PET substrates under various conditions. (a)-(d) and (e)-(h) represent the GZO films deposited under various sputtering powers (30-100 W) and total gas pressures (1.0-3.0 Pa), respectively.

$\Delta R/R_0$ values of the GZO films deposited at a P_{tot} of 1.0-3.0 Pa at a constant sputtering power of 50 W are shown in Figs. 2(e)-2(h). The results show that the $\Delta R/R_0$ value decreased as P_{tot} increased up to 2.0 Pa, and then remarkably increased as P_{tot} was further increased up to 3.0 Pa.

These results could be explained by the kinetic energy of the sputtered atoms (Zn or Ga) and the bombardment of high energy particles (Ar^o, O^-). It is well known that the kinetic energy of the sputtered particles and the bombardment of the high energy particles tends to increase with increasing sputtering power and decreasing P_{tot} [7]. In the case of a low sputtering power and high P_{tot}, the kinetic energy of the sputtered particles arriving at the substrate surface is insufficient for them to migrate on the growing films. Therefore, the Zn atoms with low energy cannot adjust their bond direction and length, with the result that they do not achieve optimum bonding to the adjacent atoms. In addition, the Ga atoms incorporated in the films might be segregated into the grain boundaries or form a secondary phase of Ga_2O_3 [5, 8], which might be related to the decrease of the film durability during the cyclic bending test.

In the case of a high sputtering power and low P_{tot}, on the other hand, the bombardment of the high energy particles arriving at the film surface was increased. The increased bombardment of the high energy particles might increase both the number of defects and internal stress of the growing films [9, 10]. This would result in the films having poor durability, due to the partial detachment of the GZO films and generation of micro cracks during the cyclic bending test.

The XRD patterns of the GZO films deposited on the PET substrates under various conditions are shown in Fig. 3. All of the films revealed a preferred orientation along the (002) direction. This indicates that the GZO films are polycrystalline with a wurtzite crystal structure and a preferred orientation with the c-axis perpendicular to the substrate surface. Fig. 3(a) shows the XRD patterns for the GZO films as a function of the sputtering power at a constant P_{tot} of 2.0 Pa. As shown in Fig. 3(a), the intensity of the (002) peak increased when the sputtering power was increased from 30 W to 70 W, however, it decreased as the sputtering power was further increased up to 100 W. As a result, the strongest intensity of the (002) peak was obtained for the GZO film deposited at a sputtering power of 70 W. Fig. 3(b) shows the XRD patterns for the GZO films as a function of P_{tot} at a constant sputtering power of 50 W. As P_{tot} was increased from 1.0 Pa to 2.0 Pa, the intensity of the (002) peak increased. A (002) peak with a relatively strong intensity was obtained for the GZO film deposited at a P_{tot} of 2.0 Pa. Further increasing P_{tot} leads to a decrease in the intensity of the (002) peak. Based on the above results, two mechanisms can be suggested to explain the effect of the sputtering power and P_{tot} on the crystallinity of the films.

One is the damage to the film caused by the bombardment

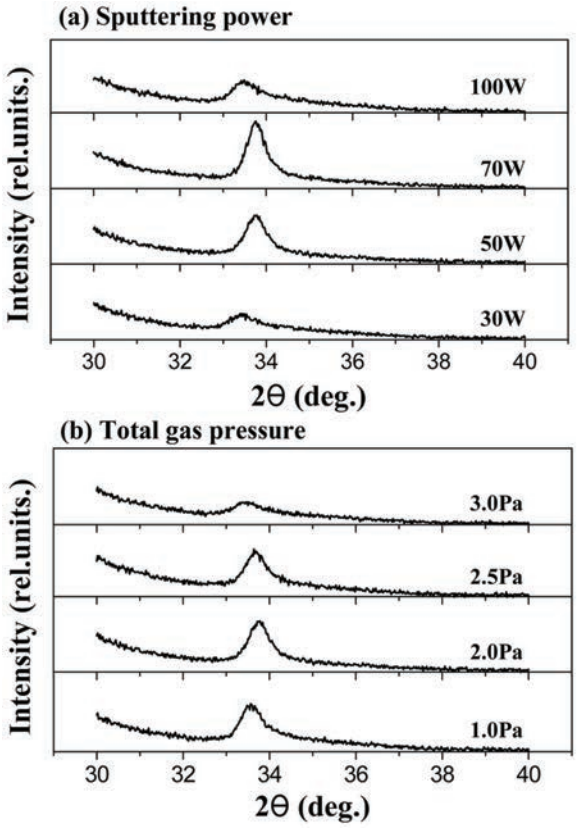

Fig. 3. XRD patterns for GZO films deposited at different (a) sputtering powers (30-100 W) and (b) total gas pressures (1.0-3.0 Pa).

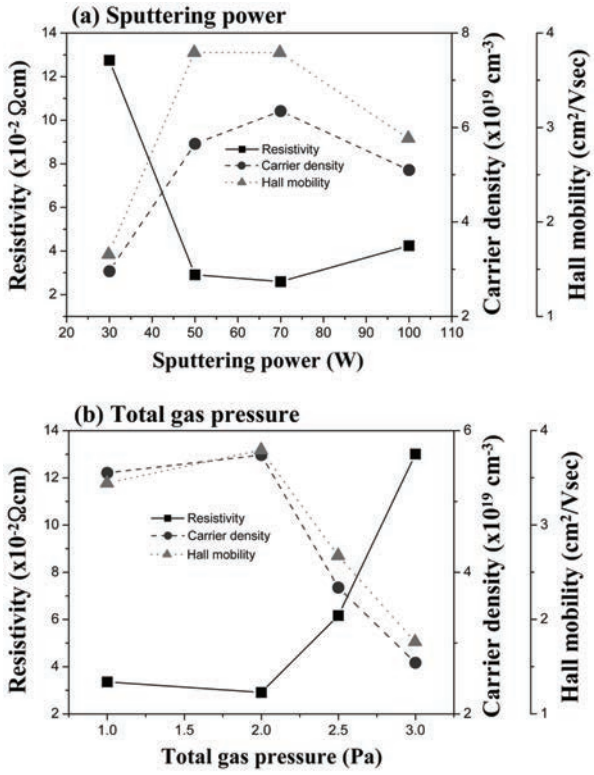

Fig. 4. Resistivity, carrier density and Hall mobility of GZO films deposited at various (a) sputtering powers (30-100 W) and (b) total gas pressures (1.0-3.0 Pa).

of the high energy particles (Ar^o, O^-) arriving at the substrate surface. As mentioned above, by increasing the sputtering power and decreasing the value of P_{tot}, the bombardment of the high energy particles was increased [11]. Another mechanism is the kinetic energy of the sputtered atoms (Zn, Ga, O) and this energy should enhance the migration on the surface of the growing films, which would significantly affect the crystallinity of the films. By decreasing the sputtering power and increasing the value of P_{tot}, a degradation in the crystallinity was observed, due to the decrease in the kinetic energy of the sputtered atoms [9].

The resistivity, carrier density and Hall mobility of the GZO films deposited on the PET substrate at various sputtering powers and various values of P_{tot} are shown in Figs. 4(a) and 4(b), respectively. As shown in Figs. 4(a) and 4(b), a relatively low resistivity was obtained for the GZO films deposited at a sputtering power of 70 W and P_{tot} of 2.0 Pa. This is due to the increase of both the carrier density and Hall mobility. The increase in the intensity of the (002) peak indicated that the electrical properties of the GZO films were clearly improved. It is considered that the increases of the carrier density and Hall mobility may be attributed to the increase in the number of substituted Ga atoms and the decrease of the grain boundary scattering, respectively [5]. Thus, we can confirm that the electrical properties of the GZO films are likely to be strongly affected by their crystallinity.

Figure 5 shows AFM images of the GZO films deposited on the PET substrate under different conditions. The surface roughness of the GZO films was quantified by the average roughness (R_a). The R_a values of the GZO films deposited at different sputtering powers and different values of P_{tot} are shown in Figs. 5(a)-5(d) and Figs. 5(e)-5(h), respectively. Relatively low R_a values were obtained for the GZO films deposited at 70 W and 2.0 Pa. These results were

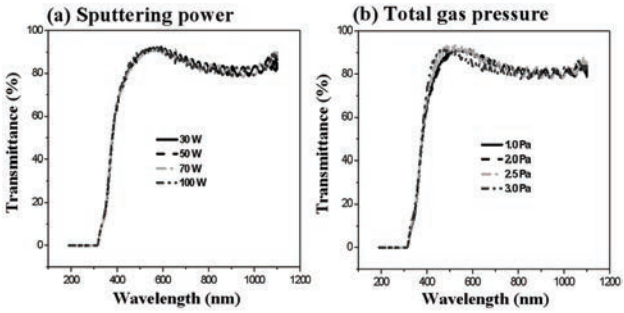

Fig. 6. Transmittance of GZO films deposited on PET substrate at various (a) sputtering powers (30-100 W) and (b) total gas pressures (1.0-3.0 Pa).

in agreement with the observed structural and electrical properties [12]. It is therefore considered that the film smoothness could be affected by both the enhancement of the migration of the sputtered atoms and a low bombardment of the high energy particles. Overall, it is also confirmed that the surface morphology and the structural and electrical properties are associated with the mechanical properties. As regards the effect of the sputtering power, although the sputtering power used to obtain the film with the optimum mechanical properties was lower than those used to obtain the films with the optimum surface morphology and optimum electrical and structural properties, this result is explained by an increase in the amount of internal stress due to the increase in the bombardment of the high energy particles [8, 9].

Figs. 6 (a) and (b) show the optical transmittances of the GZO films deposited on the PET substrate under various conditions of sputtering power and P_{tot}, respectively. The transmittances of all of the films were higher than 85% in the visible light region and no obvious difference in the transmittance was observed for the various GZO films.

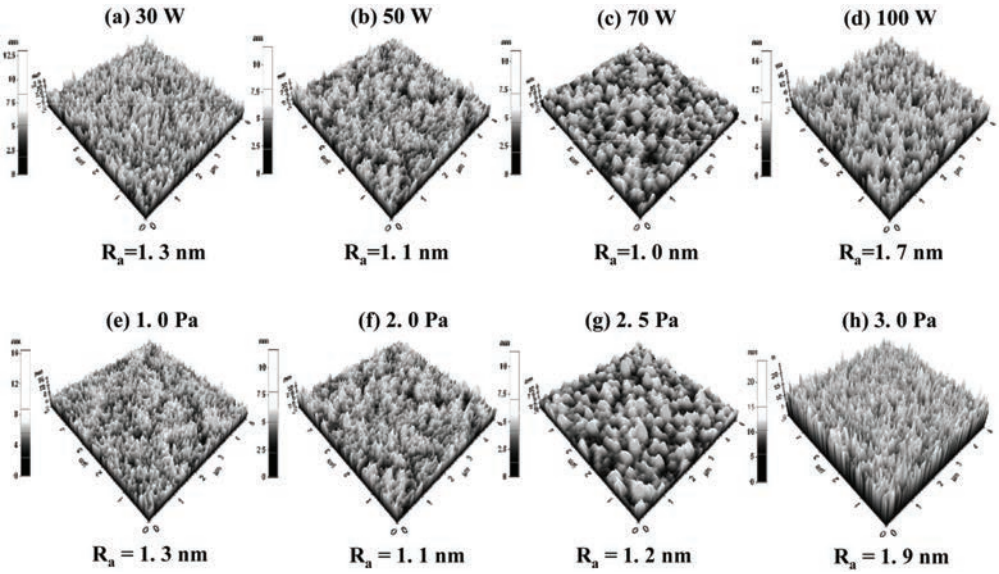

Fig. 5. AFM images of GZO films deposited under various conditions. (a)-(d) and (e)-(h) represent the GZO films deposited at various sputtering powers (30-100 W) and total gas pressures (1.0-3.0 Pa), respectively.

Conclusions

GZO films with thicknesses of 150-160 nm were successfully deposited on hard coated PET substrates using various sputtering powers and values of P_{tot} by DC magnetron sputtering without substrate heating. We made a study of the structural, electrical and optical properties and surface morphology of the GZO films. In particular, the mechanical durability of the GZO films was studied in various mechanical dynamic stress modes.

A relatively small change in resistance was observed for the GZO films deposited at a sputtering power of 50 W and P_{tot} of 2.0 Pa. The GZO films deposited at a sputtering power of 70 W and a P_{tot} of 2.0 Pa showed relatively good electrical and structural properties and surface morphology. These results could be explained by the enhancement of the migration of the sputtered atoms (Zn, Ga, O) and low bombarment energy of the high energy particles (Ar^o, O^-). In other words, the mechanical durability of the GZO films was related to their electrical and structural properties and surface morphology.

Acknowledgments

This work was supported partially by the Korea Institute of Materials Science (KIMS) and partially by grants-in-aid from the National Core Research Center Program of MOST/KOSEF (R15-2006-022-01001-0).

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