RF Magnetron sputtering으로 증착한 ZnO:Ga의 특성에 관한 연구

김호수, 김광복*, 구본강**, 박경욱**, 구경완**, 한상옥
충남대학교, 한국정보전자통신연구원*, 영동대학교**

A study on properties of ZnO:Ga thin films fabricated by RF magnetron sputtering.

H.S. Kim, K.B. Kim*, B.K. KOO**, K.Y. Park**, K.W. Koo**, S.O. Han
Chungnam Univ., Youngdong Univ.**

Abstract

Transparent conductive ZnO:Ga thin films were deposited on glass substrates using rf magnetron sputtering method for flat panel display. The ZnO:Ga films were preferentially oriented to c-axis (002) of on substrates. The surface morphology was smooth and had not porous whatever substrate temperature was. The electrical conductivity of the thin films were in the range of 1.6×10^{2} ~ 6.7×10^{3} $\Omega^{-1}cm^{-1}$ at the growth temperature from 50 to 400℃, whereas has a maximum at around 250℃. By combining of XRD and EXAFS, the crystallinity and grain size decreased with increasing substrate temperature corresponding to the reduction of the grain-boundary scattering. The optical transmittance of sputtered ZnO:Ga thin films had an improved about 86% in the UV-visible region.

Key Words : Flat panel display, Transparent electrode, sputtering, EXAFS

1. INTRODUCTION

Gallium-doped zinc oxide (ZnO:Ga), which has good electrical conductivity and high transmittance, is an interesting transparent conductive oxide (TCO) material for applications as transparent electrode including optoelectronic devices and flat panel displays[1-2]. SnO_2 and ITO have been widely investigated and used for various applications. Since ITO thin films have high transmittance in the visible range, high infrared reflection and low resistivity. However, there are required to use under environmental degradation. ZnO, as another member of this compound, has an n-type wide band gap semiconductor (Eg = 3.3eV). Un-doped ZnO has a high resistivity, but its conductivity can be controlled by doping with Al, Ga and In elements[3-5]. Various deposition method of ZnO:Ga films on various substrates have been employed by sol-gel[6], spray pyrolysis[7], chemical deposition method[8], and sputtering[9]. Among these methods, rf magnetron sputtering is more useful method because of avoiding the use of toxic gases, low cost, high stability against a argon plasma, heat cycling and growing at a low temperature with good optical and electronic properties. In addition, sputtering method of the ZnO:Ga film has a relatively high deposition rate and is well suited to the large area deposition.

In this study, the electrical, morphology, and optical properties of ZnO:Ga films deposited by rf sputtering method are described with substrate temperature.

2. EXPERIMENT

We obtained Ga doped ZnO thin films with various thickness and substrate temperature by rf magnetron sputtering. The targets used for thin film deposition were prepared by combustion method from ZnO:Ga powders with 5.0wt.% Ga. Corning 7059 glass and Si wafer substrates were placed parallel to the target surface and separated between the target and substrates. After pre sputtering for 3~5 min, sputtering deposition was carried out with a power of 100 W-fixed at a sputter Ar gas of 50 SCCM. The substrate temperature was varied from 100 to 300℃. The film thickness was controlled by deposition time and ranged from 100 to 1000nm. All samples were annealed by RTP from 300 to 700℃ with purging N_2 gas at atmosphere.

Microstructure was investigated with the scanning electron microscope. Crystallite phase and orientation were evaluated by the X-ray diffraction method with CuK_α of 1.54056Å, step size of 0.04°/s and peak ranges from 10 to 70°. Average film roughness, *R*a, of the films were characterized by atomic force microscope with scanned area 4.0×4.0㎛. The composition of the films is analysed by Auger spectroscopy. The extended X-ray absorption fine structure (EXAFS) measurements were performed at PLS on the 3C1 beam line. The electrical properties, such as electrical conductivity, the carrier concentration, the hall mobility, and the specific resistivity of the films were characterized by Hall-effect measurements and the van der Pauw method. The optical transmittance and reflectance variations were recorded with wavelength in the UV-visible range.

3. RESULT AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of θ~2θ mode for samples deposited at different substrate temperatures. All the as-grown ZnO:Ga layers were uniform and pin-hole free with thickness of approximately 1.0㎛. The X-ray diffraction data revealed that the deposited thin films were polycrystalline with a well-defined peak oriented along the (002) plane. This indicated that the grains were strongly oriented along the c axis of hexagonal wurtzite structure ZnO, perpendicular to the substrate surface. It can be observed from the spectra that the position of (002) peak was shifted towards higher 2θ values as the substrate temperature was increased.

This phenomenon suggests that the advancement of (002) peak with substrate temperature is due to the introduction of the micro-strained mismatch between the thermal expansion coefficients of the film and the substrate[10]. Also at low substrate temperature, the crystallinity of a weak (002) orientation is poor compared to more high substrate temperature which became progressively dominant at higher temperature. This is due to the improvement of the crystallinity in the films as reported elsewhere [11].

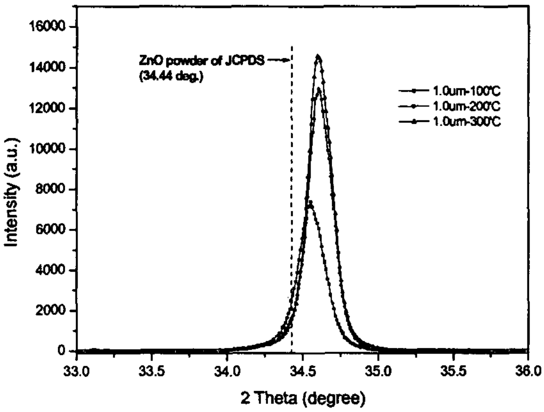

Fig. 1 ZnO:Ga peak profiles prepared at 100, 200 and 300℃ different substrate temperature.

Fig. 2 shows the surface morphology of ZnO:Ga for SEM and AFM, respectively. It is clear that all the films have columnar structure. The grain size, ranging 30 ~ 60 nm, decreases with increasing substrate temperature and data obtained from X ray analysis also indicates the same trends.

Composition of sputtered ZnO:Ga thin film for a deposited at 200℃ is given in Fig. 3. The atomic ratio of Zn/O/Ga is 49.6/46.0/4.4 from the depth profile. Through the Ga composition of depth profile, Ga is well incorporated in the ZnO matrix whatever the deposition conditions are.

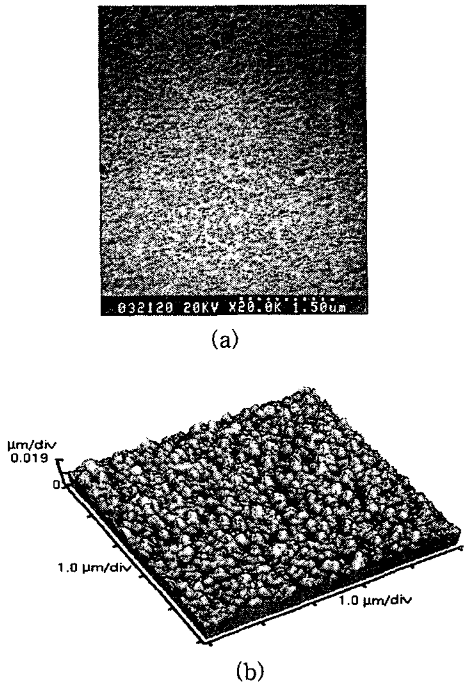

Fig. 2 SEM (a) and AFM (b) for ZnO:Ga thin films for a deposited at 200℃.

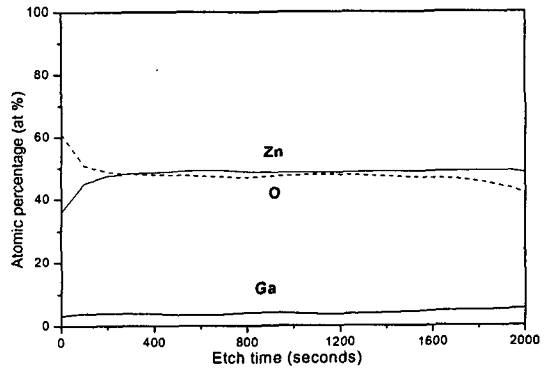

Fig. 3. Auger analysis for ZnO:Ga thin films for a deposited at 200℃.

EXAFS measurements were performed in order to verify the local structure of ZnO:Ga films and shows Zn K-edge spectrum in Fig. 4. The data analysed by comparison of the phase and amplitude in the forward Fourier transform of $\chi(k)$ spectrum of a stoichiometric ZnO:Ga film to those of the powder standards. The first peak in the Fourier transforms contains information on the oxygen nearest-neighbour of Zn atoms. The Zn to O peak positions for sputtered ZnO:Ga film is not shown at 1.974 Å. The second peak of ZnO:Ga situated at 3.324 Å (Fig. 4) corresponds to Zn Zn distance. This distance is shifted to the right scale in the literature for the würtzite form of ZnO films [12].

The electrical properties of ZnO:Ga thin films were strongly influenced by the substrate temperature at the same concentration of Ga dopant.

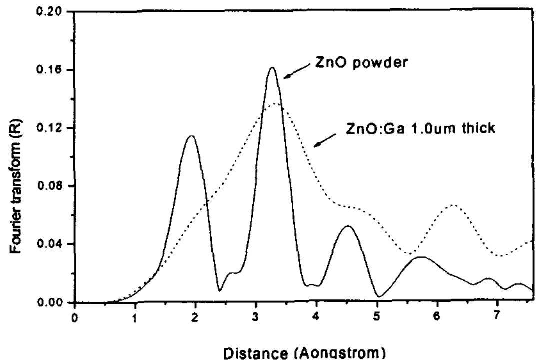

Fig. 4 Radial diffusion functions of ZnO:Ga thin films for a deposited at 200℃.

Fig. 5 shows the variation in electrical conductivity, mobility and carrier density of ZnO:Ga films with substrate temperature. The conductivity for ZnO:Ga films with a 5.0 at % Ga varied in the range $1.6\times10^{2}\sim6.7\times10^{3}\Omega^{-1}cm^{-1}$ with a variation substrate temperature from 50 to 400℃. The hall mobility and carrier density with the growth temperature is shown in Fig. 5. Both the carrier concentration and mobility initially increased with increasing substrate temperature and the mobility saturated, whereas the carrier density had a maximum at around 300℃.

The increase of electrical conductivity and mobility was mainly due to an improvement in the crystallinity and grain size as can be seen XRD data. Also, the scattering at the grain boundary reduced with increasing grain size in a barrier height. The values of conductivity, carrier density and mobility obtained in the present study are comparable with the reported values for ZnO:Ga thin films by other techniques [13].

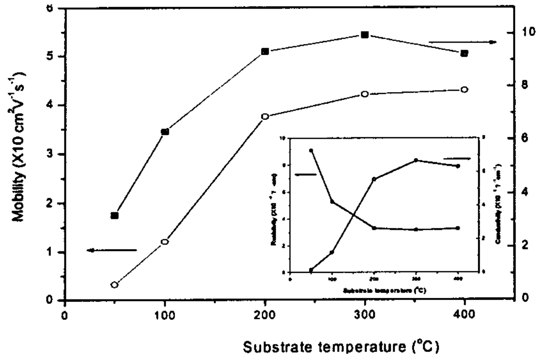

Fig. 5. Electrical conductivity, mobility, resistivity and carrier density of ZnO:Ga thin films for a deposited at different substrate temperature.

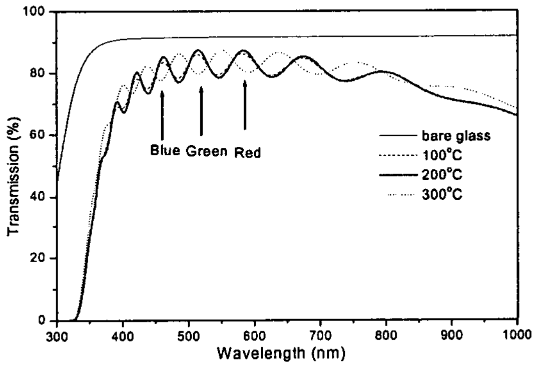

Fig. 6. Spetral transmittance of ZnO:Ga thin films for a deposited at different substrate temperature.

The optical transmittance of ZnO:Ga films with substrate temperature is shown in Fig. 6. The measured spectra include the diffuse transmittance (forward light scattering component) and diffuse reflectance (backward light scattering component). The transmittance curves were moved to short wavelength as increasing the substrate temperature. The films deposited at the substrate temperature of 200℃ had improved transmittance of about 86% in the visible range. Also this deposition temperature of sputtered ZnO:Ga films can be adopted as transparent conductive materials which shows highly at each red, green and blue wavelength.

4. CONCLUSION

ZnO:Ga thin films highly transparent to visible light and homogeneous composition were obtained by rf sputtering. The crystallinity is oriented along the (002) direction and the grain size decreased with deposition temperature. The local environment of EXAFS for doped Ga shows the 3.324 Å corresponding to zinc zinc distance. The electrical conductivity is a maximum of 6.7×10^3 Ω cm and the optical transmittance of 86% by suitably controlling the substrate temperature. Furthermore, studies for structure refinement of doped Ga is in progress and will be presented in a forthcoming article.

REFERENCE

[1] F.P. Fehlner, J. Non Cryst. Solids, 218 (1997) 360.

[2] T. Nakada, Y. Ohkubo, A. Kunioka, Jpn. J. Appl. Phys., 30 (1991) 3344.

[3] T. Minami, H. Sato, H. Sonohara, S. Takata, T. Miyata, I. Fukuda, Thin Solid Films, 253 (1994) 14.

[4] J.T. Cheung, S.R. Johnson, Aerospace Engng., 14 (1994) 7.

[5] H. Gomez, A. Maldonado, R. Asomoza, E.P. Zironi, J. Caneta Ortega, J. Palacios Gomez, Thin Solid Films, 293 (1997) 117.

[6] M.N. Kamalasanan, S. Chandra, Thin Soild Films, 288 (1996) 112.

[7] S. Zafar, C.S. Ferekides, D.L. Morel, J. Vac. Sci. Technol. A 13 (1995) 2177.

[8] J. Hu, R.G. Gordon, J. Appl. Phys., 71 (1992) 880.

[9] L.J. Meng, M.P. Dossantos, Vacuum 46 (1995) 1001.

[10] S.L. King, J.G.E. Gardeniers, I.W. Boyd, Appl. Surf. Sci. 96 98 (1996) 811.

[11] V. Craciun, J. Elders, J.G.E. Gardeniers, I.W. Boyd, Appl. Phys. Lett. 65 (1994) 2963.

[12] R.W.G. Wyckoff, Crystal Structures, Vol. 1, Interscience, New York, 1960, p. 19

[13] B.M. Ataev, A.M. Bagamadova, A.M. Djabrailov, V.V. Mamedov, R.A. Rabanov, Thin Solid Films 260 (1995) 19.