Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 38S (2012) S605–S608

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of substrate temperature on the electrical and optical properties of Ga-doped ZnO thin films fabricated by continuous composition spread

Keun Jung [a,c], Won-Kook Choi [b], Seok-Jin Yoon [a], Hyun Jae Kim [c], Ji-Won Choi [a,*]

[a] Electronic Materials Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Republic of Korea
[b] Opto-electronic Materials Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Republic of Korea
[c] School of Electrical and Electronic Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Republic of Korea

Available online 27 May 2011

Abstract

The electrical and optical properties of Ga-doped ZnO (GZO) thin films deposited at different substrate temperatures have been studied by a continuous composition spread (CCS) method. The full range of GZO compositions deposited at different substrate temperatures was explored to find excellent electrical and optical properties. Optimized GZO thin films with a low resistivity of 9.6×10^{-4} Ω cm and an average transmittance above 89% in the 400–700 nm wavelength regions were able to be formed at a substrate temperature of 100 °C. Optimized composition of the GZO thin film which had the lowest resistivity and highest transmittance was found at 0.8 wt% Ga_2O_3 doped ZnO.

Keywords: C. Electrical conductivity; C. Optical properties; D. ZnO; E. Electrodes

1. Introduction

Recently, impurity doped zinc oxide is a possible alternative to ITO due to its unique electrical and optical properties. Doped zinc oxide has good benefits for the application in FPDs because of nontoxic, inexpensive and abundant material. The group-III atoms such as B, Al, Ga, and In have been investigated as n-type dopants for ZnO because they can replace the Zn sites in the ZnO crystal and more one free electron is generated. Al-doped ZnO (AZO) thin films and Ga-doped ZnO (GZO) thin films have been widely researched. Especially, GZO thin films are more attractive than AZO thin films, because GZO thin films are more resistant to oxidation and small lattice mismatch upon doping as compared with AZO thin films. In addition, the ionic radius of Ga (0.62 Å) is larger than that of Al (0.54 Å), and is close to that of Zn (0.74 Å). The covalent bond length of Ga–O (1.92 Å) is similar to that of Zn–O (1.97 Å) [1–3].

There are many reports about GZO thin films according to a different doping concentration of Ga. However, there is still a controversy about optimized Ga doping concentration in ZnO. Thus, we investigated the full compositions of GZO deposited at different substrate temperatures to find optimized GZO composition by a continuous composition spread (CCS) method.

In this study, the full range of $Ga_xZn_{1-x}O$ was deposited on a glass substrate at various substrate temperatures of room temperature (R.T), 100, and 200 °C and evaluated electrical properties to explore optimized composition, which has excellent electrical and optical properties.

2. Experimental

Ga doped ZnO thin films were deposited on 6 in. glass substrates (eagle 2000, corning) at various substrate temperatures between R.T and 200 °C by an off-axis sputter-CCS. The off-axis sputter-CCS has three independent radio frequency (RF) magnetron sputtering guns. Zinc oxide (purity: 99.99%, CERAC) and Ga_2O_3 (purity 99.99%, CERAC) targets were used to explore the optimized composition of GZO. The sputtering was performed at a pressure of 2.66 Pa in a pure argon atmosphere. The ZnO and Ga_2O_3 targets were powered by using independent RF supplies (Ga_2O_3: 200 W and ZnO: 150 W) to achieve the desired composition range on the substrate.

* Corresponding author. Tel.: +82 2 958 5556; fax: +82 2 958 6720.
E-mail address: jwchoi@kist.re.kr (J.-W. Choi).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.107

The thicknesses of the thin films were examined through cross-section observation by field emission scanning electron microscope (XL-30, FEG). The crystal structures of the GZO thin films were investigated by X-ray diffraction (D/MAX-2500, RIGAKU). The electrical properties of the GZO thin films were measured using the four-point probe method (MCP-T600, Mitsubishi chemical) with an automatic probe station (19S, TEL) and Hall effect measurement system (HMS-3000, Ecopia). The optical transmittance was measured in the range of 200–900 nm by an UV/VIS spectrometer (Lambda 18, PerkinElmer).

3. Results and discussion

The growth rates and thicknesses of Ga_2O_3, ZnO and Ga_2O_3–ZnO thin films were measured by cross-sectional SEM analysis. Fig. 1 shows the thickness profiles of single Ga_2O_3, ZnO and binary Ga_2O_3–ZnO thin films deposited at RF power of 200 and 150 W for Ga_2O_3 and ZnO targets, respectively. Actually, the growth rates and thicknesses of thin films relate to the distances from the each target in the CCS system. Also, the thickness profiles of each single Ga_2O_3 and ZnO are directly related to the composition of binary Ga_2O_3–ZnO thin films as a function of position. When the distances from the target were increased, the growth rates and thicknesses were decreased as shown in Fig. 1. The thickness profile of Ga_2O_3–ZnO binary CCS film measured by SEM had a similar tendency with the sum of single Ga_2O_3 and single ZnO thickness profiles. The difference between the thicknesses of Ga_2O_3–ZnO binary CCS and the summation of Ga_2O_3 and ZnO single CCS are due to ballistically and diffusively deposited particles of Ga_2O_3 and ZnO [4].

Fig. 2 shows the resistivity of GZO-CCS thin films deposited at different substrate temperatures by the off-axis RF CCS. The inset of Fig. 2 shows a sheet resistance map of GZO-CCS thin films, because it is easy to understand about the trend of CCS thin films. Each position had different sheet resistances horizontally because of different $Ga_xZn_{1-x}O$ compositions.

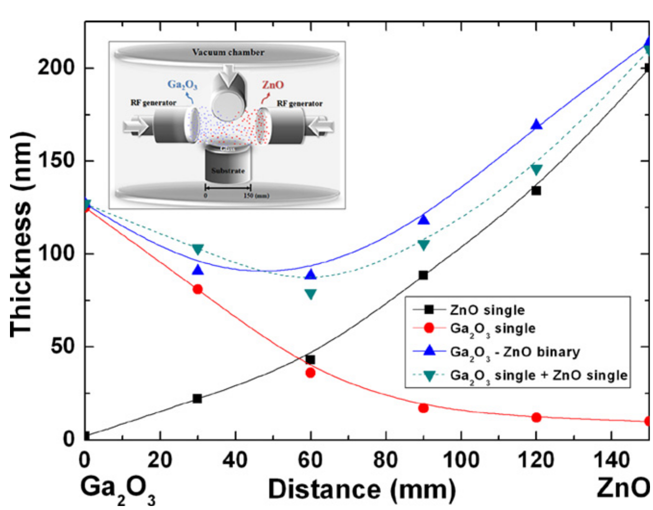

Fig. 1. Thickness profiles of Ga_2O_3–ZnO thin films deposited on the glass substrate by the off-axis sputter-CCS.

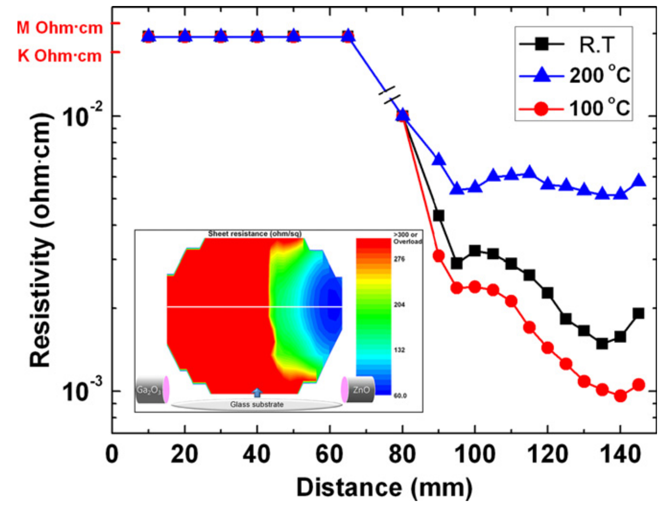

Fig. 2. Resistivity of GZO thin films as functions of substrate position (white line) deposited at R.T, 100 °C, and 200 °C by the off-axis sputter-CCS.

All GZO-CCS thin films deposited near the ZnO target had lower sheet resistance than thin films deposited near the Ga_2O_3 target because of insulating properties of Ga_2O_3. We reported compositional analysis of GZO-CCS thin films deposited at room temperature according to the position by XPS with depth profile [5]. In the paper, the Ga_2O_3 doping concentration was 13.6–0.8 wt% depending on the position 80–140 mm. As shown in Fig. 2, the resistivity of positions from 10 to 80 mm (Ga_2O_3 rich region, ≥13.6 wt% Ga_2O_3) in all GZO-CCS thin films deposited at R.T, 100, and 200 °C was higher than 1.0×10^{-2} Ω cm or overloaded but the resistivity of positions over 80 mm (Ga_2O_3 rich region, ≤13.6 wt% Ga_2O_3) was lower than 1.0×10^{-2} Ω cm. This result can be attributed to the doping concentration of Ga_2O_3 in ZnO region, which means Ga_2O_3 doped in ZnO appropriately at positions over 80 mm. At the position of 135–145 mm (0.8 wt% Ga_2O_3), the lowest resistivity of GZO-CCS thin films deposited at R.T, 100, and 200 °C was found (R.T: 135 mm, 100 °C: 140 mm, 200 °C: 140 mm). From the CCS system, we investigated the full range of GZO compositions, and found GZO thin films, which had the lowest resistivity in similar positions (135–145 mm) although they deposited at different substrate temperatures. It may be inferred that optimized GZO composition is 0.8 wt% Ga_2O_3 doped ZnO. However, they have different electrical properties according to substrate temperatures. Hence, we investigated why they have different results. Specific electrical properties of GZO-CCS thin films at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm) were measured by Hall effect measurement system as shown in Fig. 3. At the position of 140 mm which corresponds to 0.8 wt% Ga_2O_3 doped in ZnO [5] of GZO-CCS thin films deposited at 100 °C, the lowest values for the resistivity (9.6×10^{-4} Ω cm), carrier concentration (3.57×10^{20} cm^{-3}) and Hall mobility (10.9 cm^2/V s) were obtained. The decrease in resistivity is due to the increase in both carrier concentration and carrier mobility. The increase in the concentration is caused by the increase of the number of substitutional Ga^{3+} ions into Zn^{2+} sites as increasing substrate temperature up to 100 °C. This behavior can be reasonably

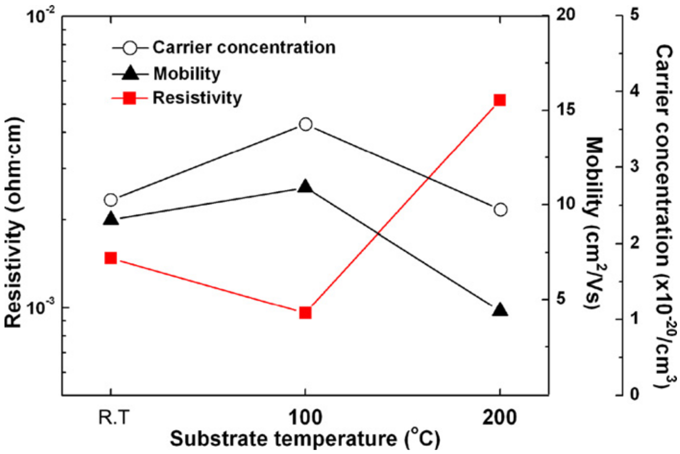

Fig. 3. Electrical properties of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm) by the off-axis sputter-CCS.

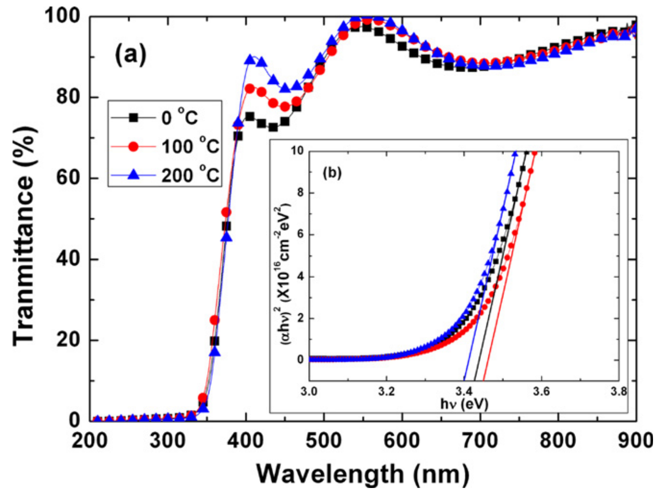

Fig. 5. (a) The optical transmittance (b) the $(\alpha h\nu)^2$ versus $h\nu$ plot of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm) by the off-axis sputter-CCS.

associated with the relative value of Zn and Ga vapor pressures. The vapor pressure of Ga remains below the chamber pressure even for the highest deposition temperature. However, the Zn vapor pressure is lower than the chamber pressure only for deposition temperatures below 100 °C. Then, at low substrate temperature film composition should be basically controlled by the atom flux impinging on the substrate from the plasma, and thin films grow with the nominal Ga content. At high substrate temperatures the growth rate is significantly reduced by Zn re-evaporation [6].

Fig. 4 shows the XRD patterns of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm). All GZO thin films exhibit a highly preferred oriented (0 0 2) and a small (0 0 4) peaks, which indicates that the films are highly oriented with their crystallographic *c*-axis perpendicular to the substrate. The GZO thin films deposited at R.T, 100 °C, and 200 °C had high 2-theta values as compared to that of ZnO thin film (34.42°), because of the increase of the number of substitutional Ga^{3+} ions into Zn^{2+} sites. This

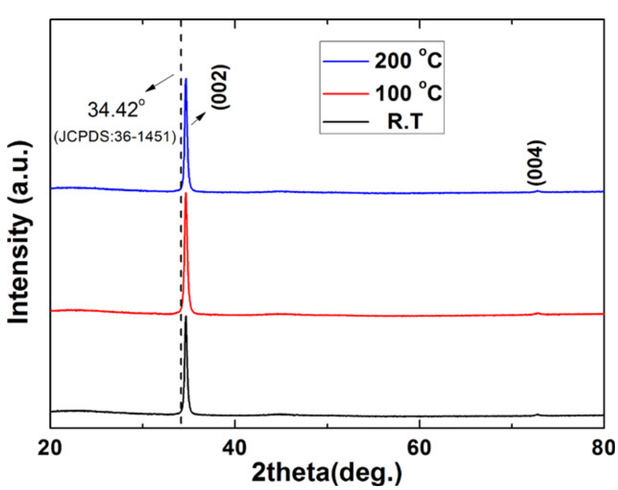

Fig. 4. XRD patterns of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm) by the off-axis sputter-CCS.

indicates that lattice parameters are decreased according to the increase of the Ga-doping concentration, because the radius of the Ga^{3+} ions (0.62 Å) is smaller than that of the Zn^{2+} ions (0.72 Å). Finally, it is inferred that much of Ga has the ability to be ionized into Ga^{3+} and substitute Zn^{2+} at a limited Ga concentration, so that it can contribute a free electron from each Ga atom [7,8].

The optical transmittance of GZO-CCS thin films deposited at various substrate temperatures between R.T and 200 °C was investigated in the wavelength from 400 to 700 nm. Fig. 5(a) shows the optical transmittance of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm). The average transmittance of all GZO-CCS thin films was over 87% in the 400 to 700 nm wavelength region. Especially, the average transmittance of the GZO thin film deposited at 100 °C, which had the lowest resistivity, was 89% in the 400 to 700 nm wavelength region. Fig. 5(b) shows the $(\alpha h\nu)^2$ versus $h\nu$ plot GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm). The optical absorption coefficient α can be obtained through $I = I_0 e^{-\alpha t}$, where I is transmitted light, I_0 is incident light, and t is the thickness of the thin films. In the direct transition semiconductor, the absorption coefficient (α) follows the following relationship with optical band gap;

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (1)$$

where E_g is the optical band gap energy, ν is the frequency of the incident photon, h is Planck's constant, and B is a constant which related to the electron–hole mobility. The optical band gap can be determined by extrapolation of the linear region from the $(\alpha h\nu)^2$ versus $h\nu$ near the onset of the absorption edge to the energy axis. The band gap of GZO-CCS thin films deposited at R.T (135 mm), 100 °C (140 mm), and 200 °C (140 mm) were calculated to be 3.4, 3.45, and 3.42 eV, respectively. Especially, the blue shift of absorption onset (200 °C → R.T → 100 °C) is relates to increase in the carrier concentration blocking the lowest states in the conduction band, well known as the Burstein–Moss effect [9].

In this field, there are a lot of reports about optimized Ga doping concentration and growth temperature. So, we investigated the full range of GZO composition by continuous composition depending on substrate temperature. The optimized substrate temperature of GZO film was 100 °C at 0.8 wt% Ga_2O_3 doped ZnO.

4. Conclusions

The GZO-CCS thin films with various compositions were deposited on glass substrate with different substrate temperatures by the off-axis sputter-CCS. The lowest resistivity and the average transmittance at the 400–700 nm wavelength region of 0.8 wt% Ga_2O_3 doped ZnO thin film deposited at 100 °C was $9.6 \times 10^{-4}\ \Omega$ cm and 89%, respectively. This GZO thin film exhibits (0 0 2) and (0 0 4) peaks, which indicates that the films are highly oriented with their crystallographic *c*-axis perpendicular to the substrate.

Acknowledgements

This study was supported by "a grant-in-aid for R&D program (No. 10030068)" funded by the Ministry of Knowledge Economy and "the R&D program for Core Converging Research Center Program (no. 2009-0082023)" funded by the Ministry of Education, Science and Technology, Republic of Korea.

References

[1] K. Ellmer, Resistivity of polycrystalline zinc oxide films: current status and physical limit, Journal of Physics D: Applied Physics 34 (2001) 3097–3108.

[2] V. Assuncao, A. Marques, H. Aguas, I. Ferreira, M.E.V. Costa, R. Martins, E. Fortunato, Influence of the deposition pressure on the properties of transparent and conductive ZnO: Ga thin-film produced by r.f. sputtering at room temperature, Thin Solid Films 427 (2003) 401–405.

[3] B.T. Lee, T.H. Kim, S.H. Jeong, Growth and characterization of single crystalline Ga-doped ZnO films using rf magnetron sputtering, Journal of Physics D: Applied Physics 39 (2006) 957–961.

[4] P.A. Sánchez, T. Sintes, J.H.E. Cartwright, O. Piro, Influence of microstructure on the transitions between mesoscopic thin-film morphologies in ballistic-diffusive models, Physical Review E 81 (2010) 011140.

[5] K. Jung, W.-K. Choi, S.-J. Yoon, H.J. Kim, J.-W. Choi, Electrical and optical properties of Ga doped zinc oxide thin films deposited at room temperature by continuous composition spread, Applied Surface Science 256 (2010) 6219–6223.

[6] J.A. Sans, J.F. Sánchez-Royo, V. Barber, M.A. Hernández-Fenollosa, B. Marí, A. Segura, Correlation between optical and transport properties of Ga-doped ZnO thin films prepared by pulsed laser deposition, Superlattices and Microstructures 39 (2006) 282–290.

[7] H.T. Cao, Z.L. Pei, J. Gong, C. Sun, R.F. Juang, L.S. Wen, Transparent conductive Al and Mn doped ZnO thin films prepared by DC reactive magnetron sputtering, Surface and Coatings Technology 184 (2004) 84–92.

[8] R.M. Ataev, A.M. Bagamadova, A.M. Djabrailov, V.V. Mamedov, R.A. Rabadanov, Highly conductive and transparent Ga-doped sapphire by CVD, Thin Solid Films 260 (1995) 19–20.

[9] E. Burstein, Anomalous Optical Absorption Limit in InSb, Physical Review 93 (1954) 632–633.