Journal of Sensor Science and Technology
Vol. 21, No. 4 (2012) pp. 263-269
http://dx.doi.org/10.5369/JSST.2012.21.4.263
pISSN 1225-5475/eISSN 2093-7563

Effect of Substrate Temperature on Electrical and Optical Properties of Al Doped ZnO Thin Films by Continuous Composition Spread

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Abstract

Al doped ZnO(AZO) thin films were deposited at different substrate temperatures by a continuous composition spread(CCS) method. Various compositions of Al doped ZnO thin films deposited at substrate temperatures between 0 and 250 °C were explored to find excellent electrical and optical properties. The AZO thin film deposited at 100 °C had the lowest resistivity, 9×10^{-4} $\Omega\cdot$cm and its average transmittance at the 400 to 700 nm wavelength region was 92 %. Optimized composition of the AZO thin film which had the lowest resistivity and high transmittance was 3.13 wt% Al doped ZnO.

Keywords : Continuous Composition Spread, Transparent Conducting Oxides, Al Doped ZnO

1. INTRODUCTION

Transparent conducting oxide(TCO) films are materials, which are electrically conductive and highly transparent to visible light. TCOs have been extensively investigated because of their important technological applications in regards to many fields such as organic light emitting diodes(OLEDs), flat panel displays(FPDs), surface acoustic waves(SAW) and solar cells[1-4]. Zinc oxide (ZnO) thin films have been considered as transparent conducting films because they are more stable against hydrogen plasma, more abundant, and less expensive than indium tin oxide(ITO) which has superior electrical and optical properties in this field.

ZnO has intrinsic defects, such as Zn interstitials(Zn_i) and O vacancies(V_o). They allow non-stoichiometric ZnO to have intrinsic n-type conductivity with high electron densities. However, electrical properties of ZnO films are not good in comparison with ITO when native point defects don't affect to ZnO as donors efficiently. So, many researchers have been focused on the intentional doping in ZnO, such as Al doped ZnO(AZO) and Ga doped ZnO (GZO). Especially, Al doped ZnO films have some advantages such as high temperature stability and higher transmittance even at near infrared wavelengths compared to ITO[5]. Many researchers have reported about AZO thin films according to the different doping content of Al[6-8]. However, there is a still controversy concerning the optimized Al doping concentration in ZnO. In this study, a full range of AZO compositions and various growth temperatures of AZO thin films were investigated by continuous composition spread(CCS). CCS is a thin film growth method for various compositions on a substrate with a binary or ternary composition spread [9-13]. Full compositions of $Al_xZn_{1-x}O$ are deposited on a glass substrate at different temperature by CCS. Especially, we focused on the effect of various substrate temperatures on the physical properties of varying Al doped ZnO films by continuous composition spread. Also, their properties such as structural, electrical and optical properties were examined.

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(Received : Jun. 12, 2012, Revised : Jul. 9, 2012, Accepted : Jul. 10, 2012)

2. DESIGN

Al doped ZnO thin films were deposited on a square sample(15 cm × 2 cm)(eagle 2000, corning) at various substrate temperatures by off-axis sputter-CCS shown as Fig. 1. The off-axis sputter CCS has three independent radio frequency(RF) magnetron sputtering guns, which are located at 90° to the substrate. A zinc oxide(purity 99.99 %, CERAC) and Al_2O_3(purity 99.99 %, CERAC) targets were used to explore the superior electrical and optical properties of AZO. The sputtering chamber was pumped down to 2.66×10^{-4} Pa by a rotary pump and turbo molecular pump. The sputtering was performed at a pressure of 2.66 Pa in a pure argon atmosphere. The Al_2O_3 and ZnO targets were powered by independent RF supplies(Al_2O_3 : 300 W, ZnO : 150 W) to achieve the desired composition range on a substrate. In order to investigate the substrate temperature dependence of the electrical and optical properties of the AZO-CCS films, AZO-CCS thin films were deposited at substrate temperatures between 0 and 250 °C. The thickness of the thin films was examined through cross section observation by FE-SEM(XL-30, FEG). The crystal structure of AZO thin films was investigated by X-ray diffraction(D/MAX-2500, RIGAKU). Electrical properties of AZO thin films were measured using the four-point probe method(MCP-T600, Mitsubishi chemical) using the automatic probe station(19S, TEL) and the Hall Effect measurement system(HMS-3000, Ecopia). Optical transmittance was measured in the range of 200-900 nm by UV/VIS spectrometer(Lambda 18, Perkin Elmer) and using Eagle 2000 glass as the reference. The thickness of the thin films was examined through cross section observation by FE-SEM(XL-30 FEG field emission scanning electron microscope). The optimized composition and thickness of thin films were characterized by Rutherford backscattering spectroscopy(RBS)(6SDH2, NEC).

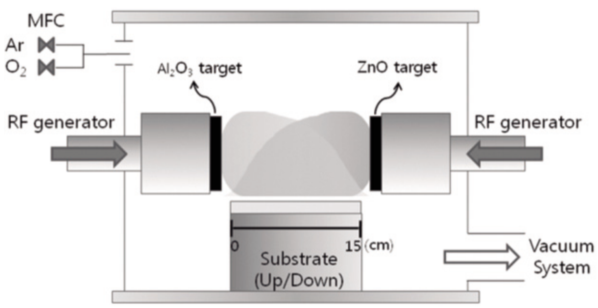

Fig. 1. Schematic diagram of the continuous composition spread (CCS) system.

3. RESULTS AND DISCUSSIONS

Fig. 2 shows the thickness profiles of single Al_2O_3, and single ZnO, Al_2O_3-ZnO thin films deposited at an RF power of 300 and 150 W for Al_2O_3 and ZnO targets, respectively. The thickness profiles for each single Al_2O_3 and ZnO are directly related to the composition of binary Al_2O_3-ZnO films as a function of position. The deposition rates and thickness of single Al_2O_3 and ZnO thin films were measured by cross-sectional SEM analysis. In the off-axis sputter-CCS system, the deposition rates and thickness of thin films relate to the distances from the target. When the distances from the target were increased, the deposition rates and thickness were decreased as shown in Fig. 2. The thickness profile of Al_2O_3-ZnO binary CCS film measured by SEM had a similar tendency with the sum of single Al_2O_3 and single ZnO thickness profiles, which were measured by SEM. The difference between the thickness of Al_2O_3-ZnO binary CCS and the summation of Al_2O_3 and ZnO single CCS is due to the ballistically and diffusively deposited particles of Al_2O_3 and ZnO[14].

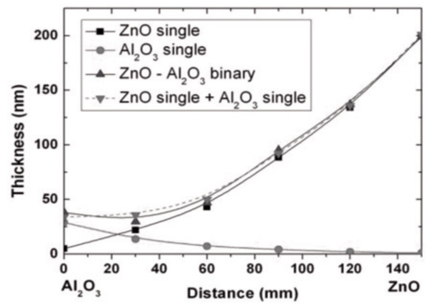

Fig. 2. Thickness profile of ZnO-Al_2O_3 thin films on a glass substrate by off-axis sputter-CCS.

Fig. 3(A) shows sheet resistance maps of AZO-CCS thin films deposited at various substrate temperatures between 0 and 250 °C. Each position of the sheet resistance map had a different value horizontally because of their different Al doped ZnO compositions. Especially, the resistivity of the areas from 0 to 9 cm for all thin films were higher than 1.0×10^{-2} $\Omega \cdot$ cm or overloaded because of the Al_2O_3 thickness which has insulating properties(Al_2O_3 rich region). However, the resistivity of areas from 9 to 15 cm of all thin films except those deposited at 200 and 250 °C were lower than 1.0×10^{-2} $\Omega \cdot$ cm (ZnO rich region doped with Al_2O_3 appropriately). We focused on areas of AZO thin films deposited near the ZnO target because the purpose of this study is to find excellent electrical properties by continuous composition spread. We indicated a red circle(position of 10 cm) on sheet resistance maps of AZO-CCS thin films because they had the lowest sheet resistance in Fig. 3(A). Fig. 3(B) shows the resistivity(position of 10 cm for each AZO-CCS thin film) of AZO thin films prepared at substrate temperatures between 0 and 250 °C. It was found that the resistivity decreased as the substrate temperature increased to 100 °C. At this temperature, the lowest values for the resistivity(9

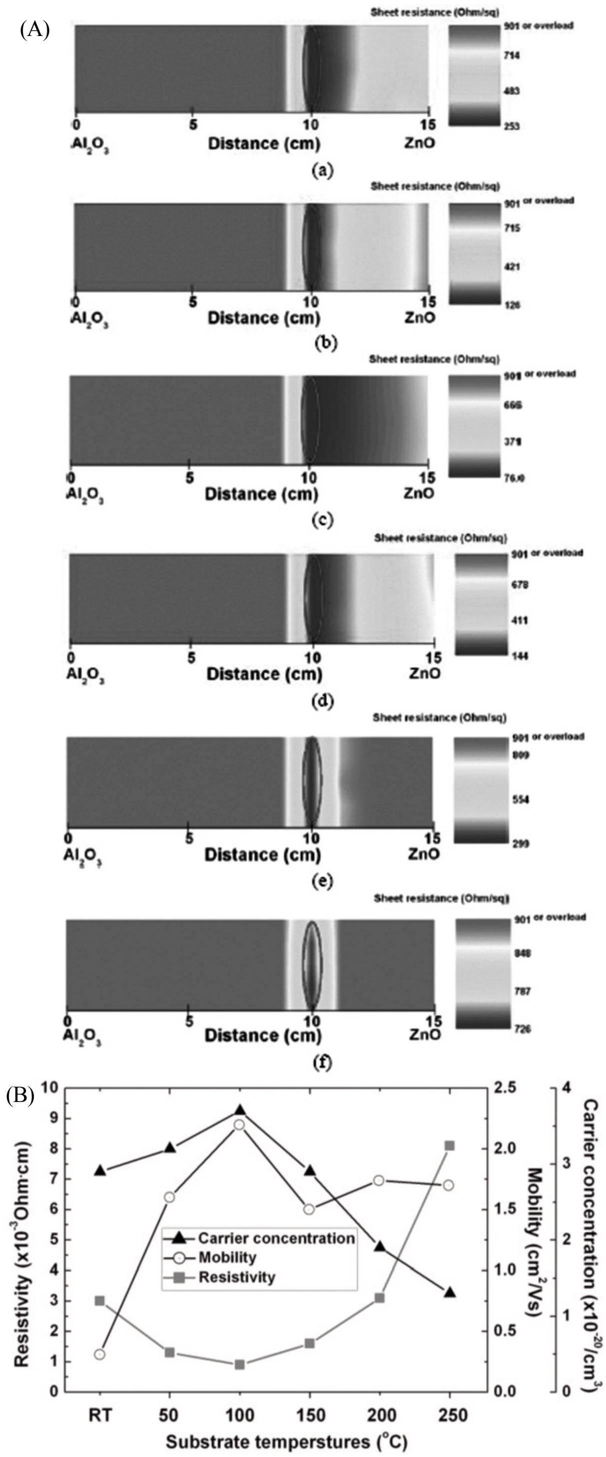

Fig. 3. (A) Sheet resistance map (B) resistivity (position of 10 cm) of AZO-CCS thin films deposited at various substrate temperatures ; (a) R.T., (b) 50 °C, (c) 100 °C, (d) 150 °C, (e) 200 °C, (f) 250 °C

$\times 10^{-4}$ $\Omega \cdot$ cm), carrier concentration(3.7×10^{20} cm^{-3}) and Hall mobility(2.2 $cm^2/V \cdot s$) were obtained. On the other hand, it was observed that the resistivity increased as the substrate temperature increased above 100 °C. The increase in the concentration is caused by the increase in the number of doped Al^{3+} ions into the Zn^{2+} sites when increasing substrate temperature up to 100 °C. This behavior can be reasonably associated with the relative value of Zn and Al vapor pressures. The vapor pressure of Al remains below the chamber pressure even at the highest deposition temperature. However, the Zn vapor pressure is lower than the chamber pressure only for deposition temperatures below 100 ºC. Then, at a low substrate temperature film composition should be basically controlled by the atom flux impinging on the substrate from the plasma, thus allowing thin films to grow with the nominal Al content. At high substrate temperatures the growth rate is significantly reduced by Zn re-evaporation[15].

Fig. 4 shows the XRD patterns(position of 10 cm for each AZO-CCS thin film) of AZO thin films prepared at substrate temperatures between 0 °C and 250 °C. All AZO thin films deposited at substrate temperatures between 0 and 250 °C exhibit a highly preferred oriented (002) and a small (004) peak, which indicates that the films are highly oriented with their crystallographic c-axis perpendicular to the substrate. This can be inferred that the Al atoms dope the Zn site in the hexagonal lattice or probably segregate to the non-crystalline region in grain boundaries and form the Al-O bond. It is believed that much of Al is able to be ionized into Al^{3+} and dope the Zn^{2+} site, so that it can contribute a free electron from each Al atom[16]. The best crystallinity was observed for the AZO thin film deposited at 100 °C. Above 100 °C, the intensity of the (002) peak decreased rapidly with increasing substrate temperatures because of the excess and difference regarding the Zn addition into AZO thin films[6].

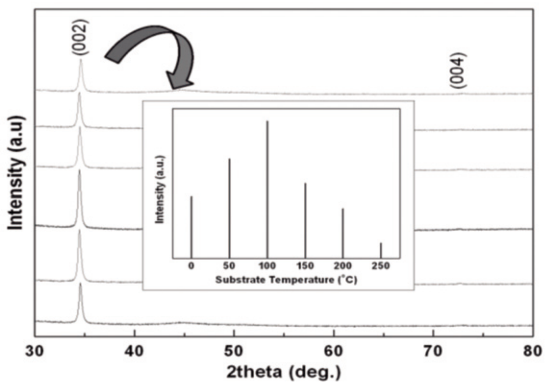

Fig. 4. XRD patterns of AZO-CCS thin films deposited at different substrate temperatures from 0 °C(bottom) to 250 °C(top), by turns.

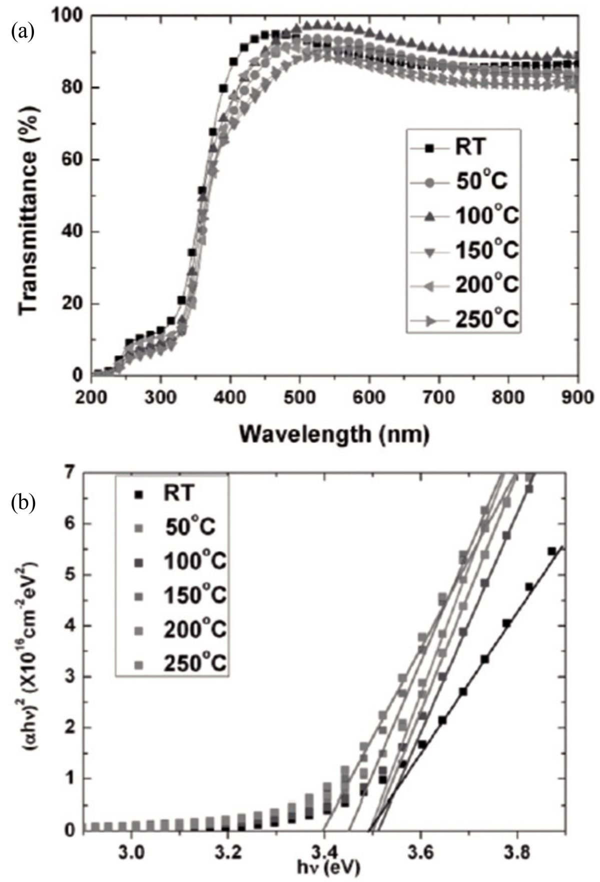

Fig. 5. (a) The optical transmittance (b) the α^2 versus hν plot of AZO-CCS thin films deposited at different substrate temperatures between 0 °C and 250 °C.

Fig. 5(a) shows the optical transmittance of AZO thin films (position of 10 cm for each AZO-CCS thin film) deposited at substrate temperatures between 0 and 250 °C. The average transmittance of all AZO thin films was over 84 % in the 400 nm to 700 nm wavelength region. Also, the average transmittance of AZO thin film deposited at 100 °C which had the lowest resistivity was 92 % in the 400 nm to 700 nm wavelength region.

Fig. 5(b) shows the $(\alpha h\nu)^2$ versus hν plot of AZO thin films(position of 10 cm for each AZO-CCS thin film) deposited at substrate temperatures between 0 and 250 °C. The optical absorption coefficient α can be obtained through $I = I_0e^{-\alpha t}$, where I is the intensity of transmitted light, I_0 is the intensity of 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 the

$$\text{optical band gap ; } \alpha h\upsilon = B(h\upsilon - E_g)^{1/2} \quad (1)$$

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 is related to the electron-hole mobility. The optical band gap can be determined through extrapolation of the linear region from the $(\alpha h\nu)^2$ versus hν near the onset of the absorption edge to the energy axis. The band gap of the AZO thin film deposited at 100 °C was found to be 3.5 eV. Especially, the absorption onset for the increase of substrate temperatures up to 100 °C is slightly blue shifted which is associated with the increase in the carrier concentration blocking the lowest states in the conduction band, well known as the Burstein-Moss effect[17, 18].

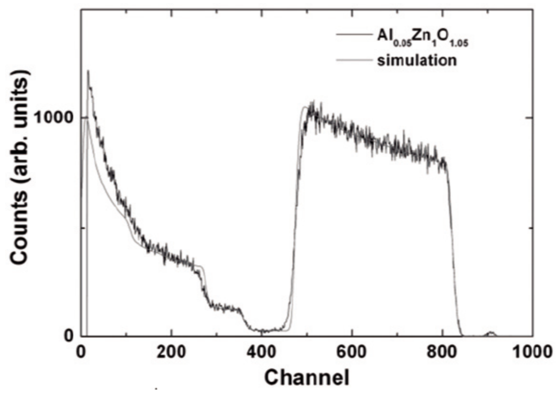

Fig. 6. 2 MeV $^4He^{++}$ Rutherford backscattering spectrum of 740 nm thick AZO thin film(position of 9 cm).

Fig. 6 shows that the compositional analysis was performed by Rutherford backscattering spectroscopy (RBS) for the 740 nm thick AZO film(position of 10 cm) which had the best electrical and optical properties. RBS was carried out using 2 MeV $^4He^{++}$ particles with a scattering angle of 170°. The composition of AZO film, 3.13 wt.% Al doped ZnO, was obtained from the RUMP code simulation.

In this field, there are a lot of reports about the optimized Al doping concentration and growth temperature. Thus, we investigated the full range of AZO compositions by continuous composition spread depending on substrate temperatures. Finally, the optimized substrate temperature of AZO film was 100 °C at 3.13 wt.% Al doped ZnO.

4. CONCLUSIONS

AZO thin films with varying substrate temperatures by the CCS method were investigated. The lowest resistivity and average transmittance at the 400 to 900 nm wavelength region of AZO thin film deposited at 100 °C was 9×10^{-4} $\Omega \cdot$ cm and 92 %, respectively. This AZO thin film exhibits (002) and (004) peaks, which indicates that the films are highly oriented with their crystallographic c-axis perpendicular to the substrate. The best crystallinity was observed for the AZO thin film deposited at 100 °C. The optimized composition (the lowest resistivity and highest transmittance) of the AZO thin film was 3.13 wt% Al_2O_3 doped ZnO.

ACKNOWLEDGMENT

This study was supported by “the Core Technology of Materials Research and Development Program(No. 10041 232) funded by the Ministry of Knowledge Economy, Republic of Korea.

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