

Influence of the aluminum and indium concentrations on the electrical resistivity and transmittance properties of InAlZnO thin films

Chanseok HONG, Hohyeong KIM, Hyoun Woo KIM, Namhee CHO, Ilhang LEE,* Ikmo LEE** and Chongmu LEE†

Department of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

*Department of Information and Communication, Inha University, Incheon 402-751, Korea

**Department of Chemistry, Inha University, Incheon 402-751, Korea

InAlZnO films were deposited on glass substrates by sputtering InZnO (In₂O₃-10 wt% ZnO) and AlZnO (3 wt% Al₂O₃-97 wt% ZnO) targets simultaneously at room temperature using a DC and AC magnetron cosputtering system. The concentration of Al in the film was varied by using different DC powers for sputtering the InZnO target with the AC power for sputtering the AlZnO target fixed. It has been found that the total concentration of Al and In in the InAlZnO films tends to be maintained constant below a certain Al doping concentration. It has been found that the electrical resistivity of the InZnO film can be decreased by doping Al the concentration of which is higher than a certain lower limit. The cause of the decrease in the resistivity of InZnO by doping 5.2 mol% Al are discussed. The optical transmittance has been found to be also enhanced in all the wavelength range except the range from 410-490 nm by doping 5.2 mol% Al.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : InAlZnO, Transparent conducting oxide (TCO), Resistivity, Transmittance, Cosputtering

[Received October 20, 2008; Accepted April 16, 2009]

1. Introduction

Indium tin oxide (ITO) and indium zinc oxide (IZO) are transparent conducting (TC) electrode materials that have been most widely used in flat panel displays (FPDs) and solar cells owing to their low electrical resistivities and high transmittances. However, significant efforts have been made for decades to develop new TC materials which can replace ITO and IZO for last two decades. As results of these efforts, metal-doped oxides such as Al-doped ZnO (AZO),¹⁻³⁾ Ga-doped ZnO (GZO)⁴⁻⁶⁾ and F-doped tin oxide (FTO)⁷⁻⁹⁾ as well as multilayer TC oxides (TCOs) consisting of oxide/metal/oxide such as ZnO/Ag/ZnO,¹⁰⁾ ITO/Ag/ITO,¹¹⁾ ITO/CuAg/ITO,¹²⁾ AZO/Al/ZnO¹³⁾ have been developed as substitutes for ITO and IZO. There have been also many reports in quaternary TCOs such as InGaZnO¹⁴⁾ in recent years. For example, Takagi et al.¹⁴⁾ has recently reported development of a transparent thin film transistor (TFT) based on amorphous InGaO₃(ZnO)₃ or a-IGZO thin film. The electron mobility in the a-IGZO thin film was reported to be as high as 6-10 cm²/Vs. However, there has been almost no report on InAlZnO (IAZO) as yet.

Recently we have reported that the electrical properties of impurity-doped ZnO films can be significantly improved by using an ultrathin Al interlayer.^{13),15)} In this paper, we report influence of the Al concentration in IAZO. Al is expected to make a stronger effect on the electrical property of IZO than Ga once it is doped into the IZO film because an elemental Al has higher electrical conductivity than an elemental Ga. In this work, Al is doped into IZO by sputtering of IZO and AZO targets simultaneously, although the sputtering power of AZO is consid-

erably lower than that of IZO in this sputtering process. We selected IZO as a base material in this study since IZO has several advantages over ITO such as higher thermal and chemical stability.

2. Experimental

InAlZnO(IAZO) films were deposited on Corning 7059 glass substrates by cosputtering a 2 inch IZO (In₂O₃: 90 wt%, ZnO: 10 wt%) and a 2 inch AZO (Al₂O₃: 3 wt%, ZnO: 97 wt%) targets simultaneously. The glass surfaces were cleaned in an ultrasonic cleaner for 10 min with acetone and methanol, respectively and then blown dry with nitrogen before they were introduced into the magnetron sputtering system. The deposition chamber was initially evacuated to 1 × 10⁻⁶ Torr and oxygen (O) and argon (Ar) gas was introduced into the chamber to maintain the desired pressure (1.2 × 10⁻² Torr). The substrate temperature and the Ar/O₂ gas flow ratio were room temperature and 30 sccm : 15 sccm, respectively. The sputtering powers for the targets were varied to make three kinds of InAlZnO thin film samples with different compositions as shown in **Table 1**. The sputtering times were controlled to obtain the film thickness of 150 nm.

For these three different kinds of samples X-ray diffraction (XRD) analyses were performed (Rigaku Co., 2500PC) to investigate the crystallinity of the IAZO films. The full width at half maximum (FWHM) of ZnO (002) XRD peaks were measured from the XRD spectra to assess the crystallinity of the IAZO films. An X-ray reflectivity (XRR) technique (X PET-PRO MRD) was used to measure the TCO film thickness. The concentrations of Al in the IAZO films determined by X-ray photoelectron spectroscopy (XPS) analyses. The carrier concentration, carrier mobility and electrical resistivity of the films were determined by Hall measurement (HEM-2000). The optical

† Corresponding author: C. Lee; E-mail: cmlee@inha.ac.kr

Table 1. Sputtering Powers of the IZO and AZO Targets and the Sputtering Time for Each IAZO Thin Film Sample

Sample No.	Target		Sputtering time (min)
	IZO target RF * power (mW)	AZO target DC** current (Ampere)	
A	300	0.0	35
B	200	0.6	40
C	250	0.6	35
D	300	0.6	30

*RF-power was applied to the IZO target.

**DC-power was applied to the AZO target.

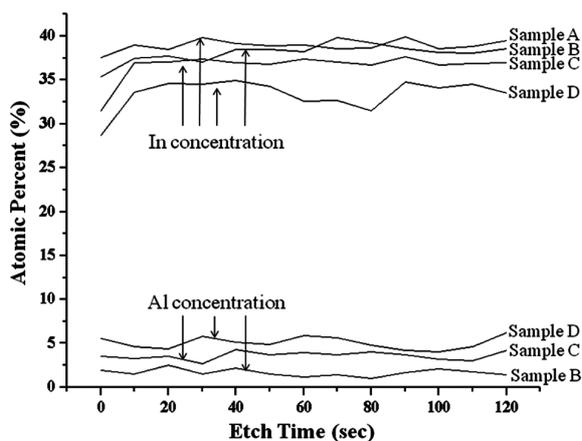


Fig. 1. Depth profiles of the IAZO samples obtained by XPS analysis.

Table 2. Al and In Concentrations in the IAZO Thin Film Samples

Sample NO.	Average Al conc. (mol%)	Average In conc. (mol%)	Average Al + In conc. (mol%)
A	0.0	38.9	38.9
B	1.7	37.4	39.1
C	3.5	36.4	39.9
D	5.2	32.7	37.9

transmittance measurements were made by using a spectrophotometer (CARY SE, VARIAN).

3. Results

Figure 1 shows the depth profiles of three different IAZO samples obtained by XPS analysis. The concentrations of Al by mol% in the IAZO thin films are plotted as functions of the sputter etching time (corresponding to the depth from the IAZO film surface). The average concentrations of Al and In in the samples read from Fig. 1 are summarized in Table 2. The carrier concentrations, carrier mobilities, and electrical resistivities of the IAZO thin films with different Al and In concentrations are plotted as functions of the Al concentration in Fig. 2. The resistivity of the IAZO thin film increases as the Al concentration increases from 0 mol% (sample A) to 1.7 mol% (sample B), but it decreases as the Al concentration increases from 1.7 mol% (sample B) to 3.5 mol% (sample C) and it decreases further as the Al concentration increases from 3.5 mol% (sample C) to 5.2 mol% (sample D). Here it should be noted that the resistivity of sample

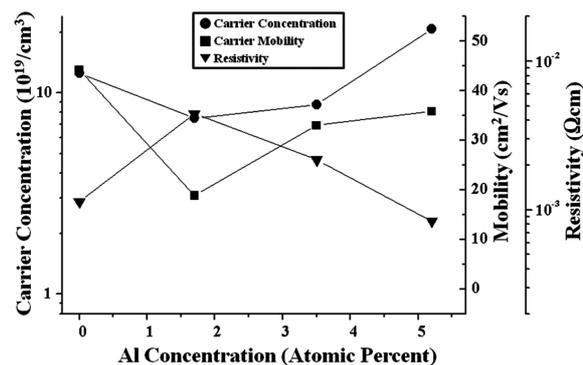


Fig. 2. Carrier concentration, carrier mobility and electrical of each IAZO film as a function of the Al doping concentrations.

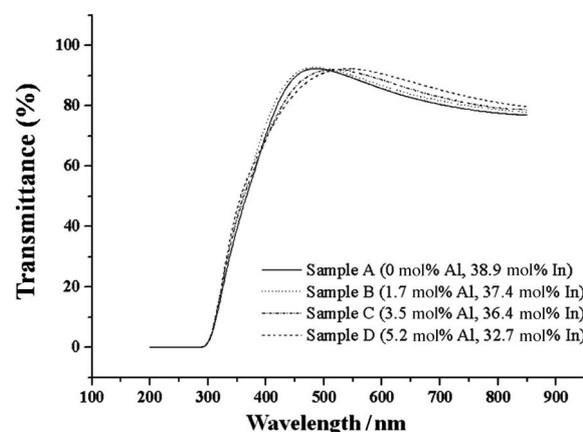


Fig. 3. Optical transmittance spectra of the IAZO thin films with different Al doping concentrations.

D is lower than that of sample A. This result suggests that we can lower the resistivity of an IZO thin film by adding a proper amount of Al to the film as a dopant. According to the Hall measurement result in Fig. 2, the optimum Al doping concentration is 5.2 mol% in the concentration range that we investigated in this study. Of course, further study using samples with Al concentrations higher than 5.2 mol% is necessary to determine the real optimum Al concentration for the lowest resistivity.

The optical transmittance spectra of the IAZO samples in the wavelength range from 200 to 850 nm is shown in Fig. 3. We can see in Fig. 3 that the transmittance of the IAZO thin film tends to increase in the spectral range higher than 510 nm. It is worthy of noting that the transmittance of sample B is higher than sample A in all the spectral range although the difference in transmittance is quite small.

The XRD spectra for the IAZO samples are shown in Fig. 4. The highest peak appearing at a 2θ of $\sim 34^\circ$ is due to ZnO (002) reflection. Al peaks as well as Al_2O_3 and In_2O_3 peaks are observed. The inset of Fig. 4 presents the full width at half maximum (FWHM) of the ZnO (002) peak. The lowest FWHM value is obtained for the Al concentration of 5.2 mol% (sample D) among samples B, C and D, which indicates that sample D is superior to samples A and B from the viewpoint of crystal quality. The AFM images of the IAZO samples are displayed in Fig. 5 and the surface roughness of the samples are also plotted as a function of the Al concentration in Fig. 6. We can see from these AFM analysis results that the IAZO thin film tends to

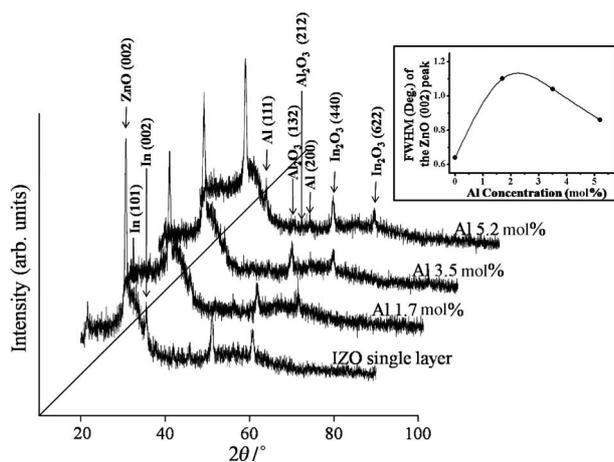


Fig. 4. XRD spectra for different IAZO thin film samples. The inset shows the FWHM of the ZnO (002) peak.

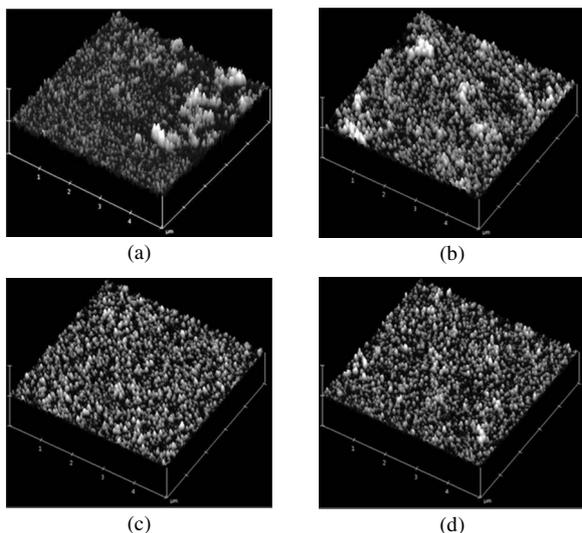


Fig. 5. AFM images of the IAZO thin films with different Al doping concentrations.

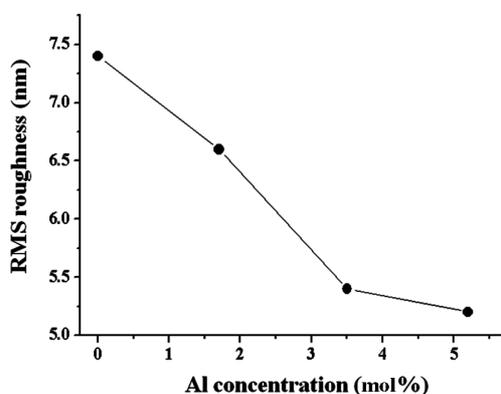


Fig. 6. Root mean square (RMS) surface roughness of the IAZO thin films deposited at room temperature as a function of the Al doping concentration.

become smoother as the Al concentration increases.

4. Discussion

The reason why we can lower the resistivity of an IZO thin film by adding a proper amount of Al as a dopant seems to be that we can substantially increase the electron concentration without sacrificing the electron mobility. According to the Hall measurement result in Fig. 2, the electron concentration of sample D ($2.08 \times 10^{20} \text{ cm}^{-3}$) is higher than that of sample A ($1.25 \times 10^{20} \text{ cm}^{-3}$) although the electron mobility of sample D ($35.81 \text{ cm}^2/\text{Vs}$) is lower than that of sample A ($44.20 \text{ cm}^2/\text{Vs}$). In other words, the resistivity is decreased by doping 5.2 mol% Al into IZO, which is mainly attributed to an increase in the Al concentration. The resistivity tends to be rather increased by doping small amounts of Al as in samples B (1.7 mol% Al) and C (3.5 mol% Al), but the resistivity seems to be decreased by doping a large amount of Al as in sample D (5.2 mol% Al).

In 2002 Tominaga et al.¹⁷⁾ reported the influence of Al and Sn impurities in the structural and electrical properties of amorphous IZO films. According to their report, addition of Al or Sn impurities to a-IZO film extends the level of Zn content where the amorphous structure appears and leads to a low-resistivity amorphous film. On the contrary, In 2006 Ito et al.,¹⁸⁾ reported that N-type impurity doping such as Sn, Al or F by 0.1–3 % could not lead to the increase in the carrier concentration in IZO. Therefore, we may say that our result contradicts to neither Tominaga et al.'s report that the resistivity of IZO is decreased by doping Al nor Ito et al.'s report that the resistivity of IZO is not increased by doping 0.1–3 mol% Al.

The reason why the electron mobility does not decrease much even if the Al doping concentration substantially increased from 0 mol% (sample A) to 5.2 mol% (sample D) may be explained as follows:

(1) As can be seen in the inset of Fig. 4, the FWHM of sample D is smaller than those of sample B and C although it is somewhat larger than those of sample A. This indicates that the crystal quality of the IAZO thin film starts to be enhanced again as the Al doping concentration exceeds a certain limit (~2.0 mol%). It is well known that the carrier mobility increases as the crystal quality is enhanced.

(2) Figures 5 and 6 show that the surface roughness of the IAZO thin film tends to decrease all the way through the Al concentration range below 5.2 mol% as the Al concentration increases. It is also well known that surface scattering occurs less in thin films with smoother surface or interface. In turn, less surface scattering will result in higher carrier mobility.

(3) Table 2 indicates that the In concentration in IZO tends to decrease as the Al doping concentration increases. We made every effort to increase both Al and In concentrations simultaneously by doping different amounts of Al into IZO, yet we failed. We strongly feel that the total concentration of Al and In tends to be maintained almost constant within a certain Al concentration limit but that the total concentration of Al and In will probably decrease if the Al doping concentration exceeds the upper limit. However, if we compare the sum of the Al and In concentrations in different samples listed in Table 2, we will see that the sum of the Al and In concentrations in sample D is lower than that in sample A whereas those in samples B and C are higher than in sample A. When we dope Al into IZO, the electron concentration increases since Al generates conduction electrons more easily than In (Al has a higher electrical conductivity than In), but the electron mobility decreases due to impurity scattering. However, in the case of heavy Al doping (sample D)

the electron mobility is not increased as we anticipate since impurity scattering occurs less significantly because of the lower total concentration of Al and In.

Besides electrical conductivity, optical transmittance is also an important property that a transparent conducting film should have. Figure 3 indicates that we do not have to worry about optical transmission in the case of Al doping in IZO. The transmittance of sample D (5.2 mol% Al) is substantially higher than that of sample A (0 mol% Al) in most visible light region ($\lambda > 490$ nm) although the former is lower than the latter in a limited range of wavelength ($410 < \lambda < 490$ nm). The enhancement in the optical transmittance of IZO by Al doping may be due to the lower absorbance of Al than that of In. As can be seen in Table 2, the In concentration in the IAZO thin film decreases as the Al doping concentration increases. In general, the optical transmittance of a solid increases as its optical absorbance and reflectance decreases. It is well known that the optical absorbance of Al is much lower than that of In in most spectral region¹⁶⁾ although the reflectance of Al is higher than that of In.¹⁶⁾ The lower absorbance means higher transmittance. Therefore, sample D with a higher Al concentration and a lower In concentration has a higher transmittance than sample A with a lower Al concentration and a higher In concentration.

5. Conclusions

InAlZnO films were deposited on glass substrates by sputtering InZnO (In₂O₃-10 wt% ZnO) and AlZnO (3 wt% Al₂O₃-97 wt% ZnO) targets simultaneously at room temperature using a magnetron cosputtering system with both DC and AC sputtering guns. The concentration of Al in the film was varied by using different DC powers for sputtering the InZnO target with the AC power for sputtering the AlZnO target fixed. It has been found that the sum of the Al and In concentration in the InAlZnO films tends to be maintained constant in the Al doping concentration range below a certain limit. The electrical resistivity of the InAlZnO film tends to increase as the Al doping concentration increases up to 1.7 mol% but the resistivity tends to decrease with further increases in the Al doping concentration. The lower resistivity of the InAlZnO film with an Al concentration of 5.2 mol% in comparison with that of InZnO film is mainly attributed to the higher electron concentration and the electron mobility not much lower than that of the InZnO film. The electron mobility increases as the doping concentration increases from 1.7 mol% to 5.2 mol%, which is due to the enhancement in the crystal

quality and the decrease in the surface roughness of the InAlZnO film with an increase in the Al doping concentration. The optical transmittance has been found to be also enhanced by doping 5.2 mol% Al in all the spectral range except the range from 410 to 490 nm.

Acknowledgement This work was supported by INHA UNIVERSITY Research Grant.

References

- 1) F. O. Adurodija, H. Izumi, T. Ishihara, H. Yoshioka, H. Matsui and M. Motoyama, *Jpn. J. Appl. Phys.*, **38**, 2710 (1999).
- 2) K. Yim and C. Lee, *Cryst. Res. Technol.*, **41**, 1198-1202 (2006).
- 3) K. Yim, H. W. Kim and C. Lee, *J. Electroceram.*, **17**, 875-877 (2006).
- 4) H. Gomez, M. Olvera and L. Dela, *Mater. Sci. Eng.*, **B134**, 20-26 (2006).
- 5) S. Kim, J. Jeon, H. W. Kim, J. G. Lee and C. Lee, *Cryst. Res. Technol.*, **41**, 1194-1197 (2006).
- 6) K. Yim, H. W. Kim and C. Lee, *Mater. Sci. Technol.*, **23**, 108-112 (2007).
- 7) K. H. Yoon and J. S. Song, *Solar Energy mater. Solar Cells*, **28**, 317-327 (1993).
- 8) D. Zaonk, Y. Zaatar, A. Khoury, C. Llinares, J-P. Charles and J. Bechara, *J. Appl. Phys.*, **87**, 7539-7543 (2000).
- 9) T. Kawashima, T. Ezure, K. Odaka, H. Matsui, K. Goto and N. Tanabe, *J. Photochem. Photobiol.-A*, **164**, 199 (2004).
- 10) G. Fangl, D. Li and B. L. Yao, *Instit. Phys. Publish., J. Phys. D: Appl. Phys.*, **35**, 3096 (2002).
- 11) E. Kusamo, J. Kauaguchi and K. Enjoiji, *J. Vac. Sci. Technol.*, **A4**, 2907 (1986).
- 12) M. Bender, W. Seeling, C. Daube, H. Frankenberger, B. Ocker and J. Stollenwerk, *Thin Solid Films*, **326**, 67 (1998).
- 13) W. Lee, R. P. Dwivedi, C. Hong, H. W. Kim, N. Cho and C. Lee, *J. Mater. Sci.*, **43**, 1159-1161 (2008).
- 14) A. Takagi, K. Nomura, H. Ohta, H. Yanagi, T. Kamiya, M. Hirano and H. Hosono, *Thin Solid films*, **486**, 38-41 (2005).
- 15) C. Lee, R. P. Dwivedi, W. Lee, C. Hong, W. I. Lee and H. W. Kim, *J. Mater. Sci.: Mater. Electron.*, **19**, 981-985 (2008).
- 16) E. D. Palik (Ed), "Handbook of Optical Constants of Solids," Academic Press (1985).
- 17) K. Tominaga, T. Takao, A. Fukushima, T. Moriga and I. Nakabayashi, *Vacuum*, **66**, 505-509 (2002).
- 18) N. Ito, Y. Sato, P. K. Song, A. Kaijio, K. Inoue and Y. Shigesato, *Thin Solid Films*, **496**, 99-103 (2006).