

Effects of flow rate of oxygen and substrate temperature on the characteristics of IZO thin films for OLEDs

H. K. Jeoung and K. M. Lee*

Dept. of Materials Engineering, Korea University of Technology and Education, Cheonan, Chungnam 330-708, Korea

This study examined the effects of the O₂ flow rate and the substrate temperature on the structural, electrical, and optical characteristics of the IZO thin films intended for use as anode materials in OLEDs (organic light emitting diodes). These IZO thin films were deposited by RF magnetron sputtering at room temperature and 300 °C at various O₂ flow rates. To examine the effects of O₂, the O₂ flow rate in the argon mixing gas was changed from 0.1 sccm to 0.5 sccm. IZO thin films deposited at room temperature showed an amorphous structure, whereas IZO thin films deposited at 300 °C showed a crystalline structure with an (222) preferential orientation regardless of the O₂ flow rate. The electrical resistivity of the IZO thin films increased with increasing O₂ flow rate under Ar + O₂. The change in the electrical resistivity with increasing O₂ flow rate was interpreted mainly in terms of the charge carrier concentration rather than the charge carrier mobility. The electrical resistivity of the amorphous-IZO films deposited at R.T. was lower than that of the crystalline-IZO thin films deposited at 300 °C. All the films showed an average transmittance of more than 83% in the visible range. The optical band gap of the IZO films increased with decreasing O₂ flow rate. The current density and luminance of the OLED devices with IZO thin films deposited at room temperature in 0.1 sccm O₂ ambient gas were the highest among the films examined. These properties were attributed to the improved optical band gap, which plays a major role in the OLED device performance.

Key words: IZO thin film, RF magnetron sputtering, Flow rate of oxygen gases, Substrate temperature, Optical band gap, OLED device.

Introduction

Transparent conducting oxide (TCO) thin films have been studied extensively for applications to display devices, such as liquid crystal displays (LCDs), plasma display panels (PDPs) and organic light emitting diodes (OLEDs) [1-3]. Of the TCO films, indium tin oxide (ITO) thin films have been used extensively in these devices because of their high transmittance in the visible range and low electrical resistivity [4, 5]. On the other hand, to have high electrical conductivity and high transmittance, ITO thin films must be deposited and annealed at temperatures higher than 250 °C and 300 °C, respectively. This high temperature post-annealing makes ITO films rough due to crystallization, which leads to significant deterioration of the device reliability [4, 5].

Recently, new transparent conducting oxides, such as IZO (indium zinc oxide) thin films have emerged as promising anode materials for OLEDs owing to their low deposition temperature, high work function, low resistivity, excellent chemical stability, and high transmittance over 80% in the visible spectrum [6-8]. IZO thin films can be deposited by RF magnetron sputtering, which has been used widely because of its

advantageous features including simple apparatus, high deposition rates, and low deposition temperature. The properties of IZO thin films depend strongly on the stoichiometry, microstructure, and nature of the impurities, and it is obvious that deposition processes associated with different control parameters induce slightly different characteristics in thin films [6-8]. Several groups have examined the effects of O₂ in reactive sputtering on the electrical and structural properties of TCO films [9-11]. The roles of the partial pressure of O₂ and H₂ on the structural, optical and electrical properties of RF magnetron sputtered TCO films have also been discussed [6, 12]. From these studies, it was concluded that the electrical resistivity correlates strongly with the stoichiometry of the IZO thin films. Therefore, it is interesting to study the effect of the ambient gas on the structure and electrical resistivity, especially on the charge carrier concentration and charge carrier mobility of IZO thin films. This study examined the effects of the substrate temperature on the structural, electrical, and optical characteristics of IZO thin films on the performance of OLED devices. For this purpose, Zn-doped In₂O₃ (IZO) films were deposited by RF magnetron sputtering at room temperature and 300 °C at various O₂ flow rates. The electrical resistivity and optical band gap of the IZO thin films were examined systematically. To determine the effect of the electrical resistivity and/or the optical band gap on the performance of OLED devices, organic

*Corresponding author:
Tel : +82-41-560-1320
Fax: +82-41-560-1360
E-mail: kmlee@kut.ac.kr

materials and cathode electrode were deposited sequentially on the IZO thin films. The electrical characteristics of the OLED devices, such as current density vs. voltage and luminescence vs. voltage, were measured.

Experimental

IZO thin films were deposited by RF magnetron sputtering from a target containing 90% indium oxide and 10% zinc oxide. The glass substrates (corning 7059, SAMSUNG CORNING PRECISION GLASS, KOR) were first cleaned and rinsed in deionized water. The sputtering chamber was evacuated using a turbomolecular pump to the base pressure of about 1.0×10^{-6} torr. To examine the influences of O_2 , the O_2 flow rate in the argon mixing gas was changed from 0.1 sccm to 0.5 sccm. The substrate temperature was either room temperature or 300 °C. Table 1 lists the experimental conditions for the deposition of IZO thin films.

The microstructural observations and crystal orientation of the IZO thin films were evaluated by X-ray diffraction (XRD, RIGAKU, RTP300RC) and field emission scanning electron microscopy (FESEM, JEOL, JSM7500F), respectively. The optical transmittance of the IZO thin films was measured using an ultraviolet spectrophotometer (model Cary500, Varian, KOR). The film thickness was determined using a surface profile measurement system and the electrical properties of the IZO thin films were measured using Hall Effect measurements (model HMS-3000, ECOPIA, KOR). The organic materials and cathode electrode were deposited sequentially on the TCO thin films to give a device structure of IZO/ α -NPD (N,N-Di(naphthalene-1-yl)-N,N-diphenyl-benzidine)/DPVB ((diphenylvinyl) benzene)/Alq₃/LiF/Al. DPVB was used as a blue emitting material. The electrical characteristics, such as current density vs. voltage and luminescence vs. voltage of the OLED devices, were evaluated using a spectrometer (model CS-1000A, KONICA MINOLTA SENSING INT, JPN).

Results and Discussion

XRD patterns of the IZO thin films deposited by RF magnetron sputtering are presented in Fig. 1.

Table 1. Conditions of sputtering IZO thin films.

Deposition parameters	Conditions
Target	In ₂ O ₃ /ZnO (90/10 wt.%)
Substrate	Glass (corning 7059)
Initial pressure (torr)	5.0×10^{-6}
Working pressure (torr)	6.0×10^{-3}
Film thickness (nm)	200
Substrate temperature (°C)	Room temp. and 300 °C
RF power (W)	100
Gas ambient (sccm)	Ar:40, O ₂ flow rate:0.1-0.5

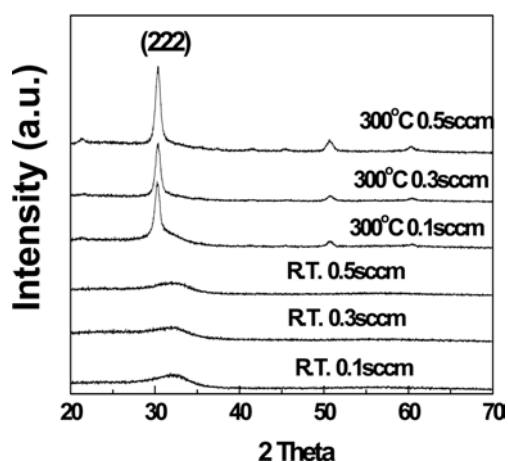


Fig. 1. XRD patterns of IZO thin films deposited at (a) room temperature and (b) 300 °C with various O_2 flow rate.

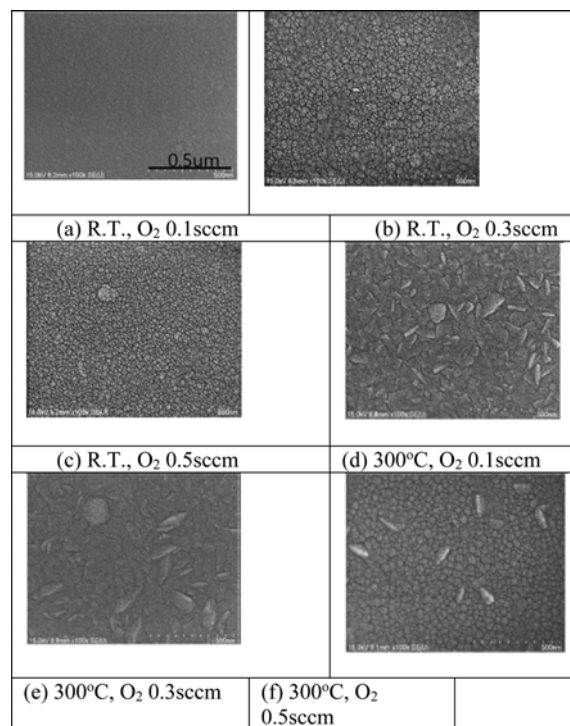


Fig. 2. Field effect scanning electron microscope images of IZO thin films with different deposition temperature and various O_2 flow rate.

The figure clearly shows that the IZO thin films deposited at room temperature were amorphous, whereas the thin films deposited at 300 °C showed a sharp (222) peak at $30.54^\circ 2\theta$, indicating that the IZO film has a (111) preferential orientation. Furthermore, with increasing oxygen concentration, the intensity of the (222) peak remained unaltered. A specific preferred orientation of the thin film can be discussed based on the strain and surface energies [13]. At thin film thicknesses, the surface energy controls growth, whereas at thick film thicknesses the strain energy predominates. Based on the above discussions, the (111) plane of IZO thin films has the lowest strain.

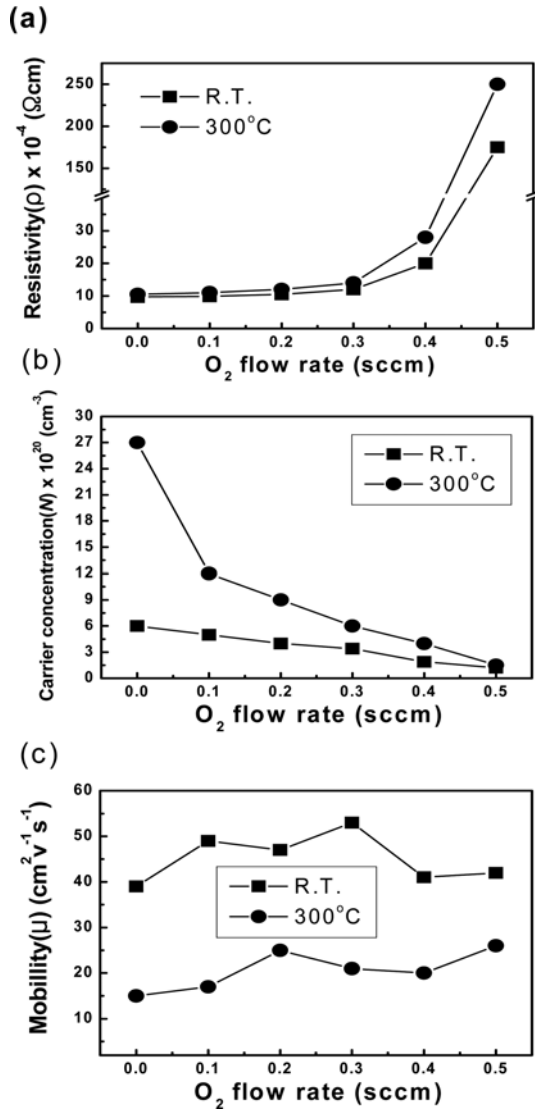


Fig. 3. (a) Resistivity (ρ), (b) charge carrier concentration (N), and (c) charge carrier mobility (μ) of IZO thin films with different deposition temperature and various O₂ flow rate.

Because the surface properties of the TCO thin films for anode materials can affect the characteristics of OLED devices [14], it is important to examine the surface morphology of the IZO thin films. Fig. 2 shows the microstructural features of the IZO thin films with different O₂ flow rates and substrate temperature. As shown in the figures, secondary phases were not observed. The grain sizes in the IZO thin films were similar regardless of the O₂ flow rate and substrate temperature. On the other hand, with increasing O₂ concentration, small cracks were observed between the grains, and the amount of hazy phases decreases (Fig. 2), which suggests that the film surface could be etched off by oxygen bombardment through a physical interaction [15]. From Figs. 1 and 2, it appears that the flow rate of oxygen gases and substrate temperature have an important effect on the physical characteristics,

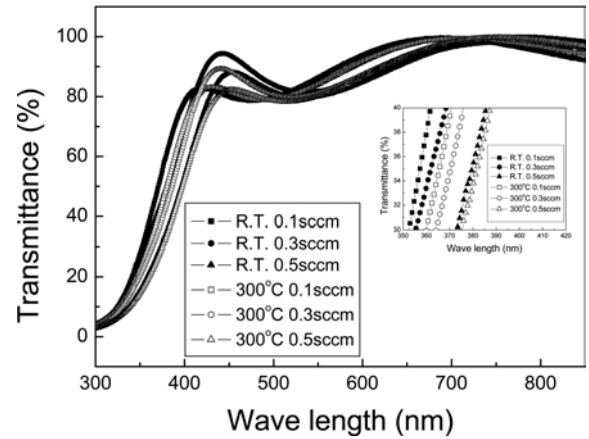


Fig. 4. Optical transmittance spectra of IZO thin films with different deposition temperature and various O₂ flow rate.

such as the crystal orientation and microstructure of the thin films.

Figure 3 shows the electrical resistivity (ρ), charge mobility (μ), and charge carrier concentration (N) of the IZO thin films with different deposition temperatures and various O₂ flow rates. As shown in the figures, the resistivity of the IZO films increased with increasing O₂ flow rate, which can be interpreted in terms of the decrease in charge carrier concentration. O₂ vacancies in In₂O₃-based TCO thin films act as donors and their presence makes the film less resistive [12]. During reactive sputtering under ambient O₂, the thin film becomes more stoichiometric and the concentration of O₂ vacancies decreases. Therefore, the electrical resistivity increases. Furthermore, the figures clearly show that the electrical resistivity of the amorphous-IZO films deposited at R.T. was lower than that of the crystalline-IZO thin films deposited at 300°C, which can be interpreted mainly in terms of the charge carrier mobility rather than the charge carrier concentration.

Figure 4 shows the optical properties of the IZO films with different deposition temperatures and various O₂ flow rates. The figure shows that the mean transmittance in the visible wavelength region was more than 85% for all IZO thin films. As the inset in Fig. 4 clearly shows, the UV absorption edge was shifted by a small wavelength with decreasing O₂ flow rate and substrate temperature, indicating broadening of the optical band gap.

The absorption coefficient, α , can be expressed by the equation, $\alpha = (1/d)\ln(1/T)$, where T is the transmittance and d is the thin film thickness (200 nm in our experiment). The optical band gap (E_{opt}) of the IZO thin films can be determined from the experimental spectra of the absorption coefficient (α) as a function of the photon energy ($h\nu$) using the following equation [16]:

$$(\alpha h\nu)^2 = C(h\nu - E_{\text{opt}}),$$

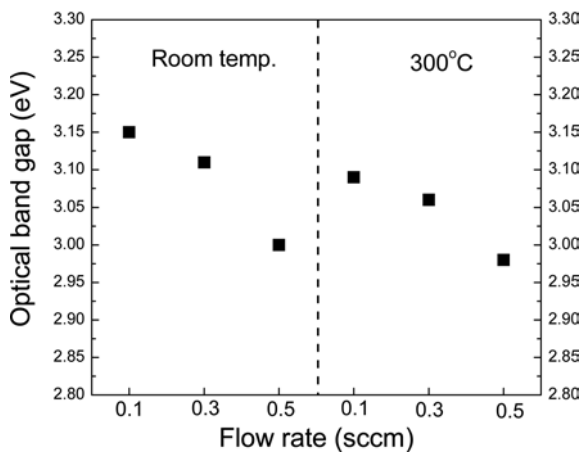


Fig. 5. Optical band gap of IZO thin films as a function of the flow rate of O_2 and the substrate temperature.

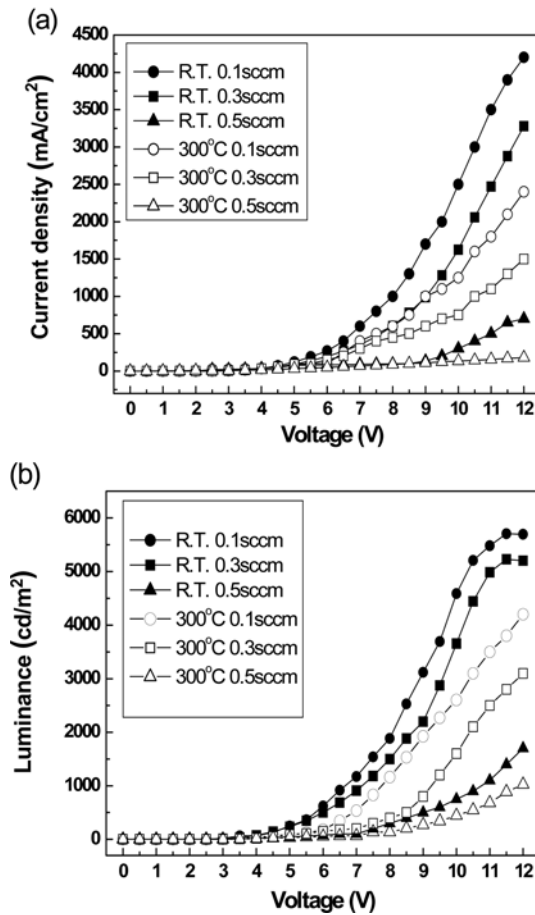


Fig. 6. (a) I-V and (b) L-V characteristics of OLED devices.

where C is a constant for a direct transition, h is Planck's constant, and ν is the frequency of the incident photon.

$(\alpha h\nu)^2$ was plotted as a function of the photon energy ($h\nu$) to estimate the band gap of the IZO thin films. Figure 5 shows the optical band gap of the IZO films, as determined from the obtained transmittance spectra. As

shown in the figure, the optical band gap of the IZO films increased with decreasing O_2 flow rate. Furthermore, the optical band gap of the IZO films deposited at 300°C was lower than that of the film deposited at room temperature at the same oxygen flow rate. An increase in the Fermi level in the conduction band of a degenerate semiconductor leads to band gap widening, which is consistent with the present experimental results [17-19].

Fig. 6 shows (a) the current density vs. voltage and (b) the luminance vs. voltage characteristics of the OLED devices with the IZO thin film deposited in various ambient gases for comparison. The device structure was IZO/ α -NPD/DPVB/ Alq_3 /LiF/Al. DPVB was used as a blue emitting material. As shown in Figure 6, the current density and luminance of the OLED devices were observed in the following order: $O_{R.T. 0.1 \text{ sccm}} > O_{R.T. 0.3 \text{ sccm}} > O_{300 0.1 \text{ sccm}} > O_{300 0.3 \text{ sccm}} > O_{R.T. 0.5 \text{ sccm}} > O_{300 0.5 \text{ sccm}}$. This order was consistent with that of the optical band gap energies of the IZO films with different deposition temperature and various O_2 flow rates (as shown in Fig. 5). If the electrical resistivity is considered to be the main parameter affecting the current density and luminance, the current density and luminance should be observed in the following order: $O_{R.T. 0.1 \text{ sccm}} > O_{300 0.1 \text{ sccm}} > O_{R.T. 0.3 \text{ sccm}} > O_{300 0.3 \text{ sccm}} > O_{R.T. 0.5 \text{ sccm}} > O_{300 0.5 \text{ sccm}}$. Therefore, the results of Fig. 6 clearly show that hole injecting ability of the IZO anode is largely dependent on the optical band gap of IZO thin films. As shown in Figure 6, the current density and the luminance of the OLED devices with IZO thin films deposited at room temperature in 0.1 sccm O_2 were the highest among the films considered. Figures 6 and 5 show that the optical band gap of IZO thin films plays a major role in OLED device performance, particularly the current density and luminance.

Conclusions

The structural, electrical and optical properties of the IZO thin films were examined systematically for use as the anode contact in OLED devices. IZO thin films were deposited by RF magnetron sputtering at room temperature and 300°C at various O_2 flow rates. The IZO thin films deposited at room temperature showed an amorphous structure, whereas the IZO thin films deposited at 300°C showed a crystalline structure with a (222) preferential orientation regardless of the O_2 flow rate. The electrical resistivity of the IZO film increased with increasing O_2 flow rate under $Ar + O_2$. The change in the electrical resistivity with increasing O_2 flow rate was interpreted mainly in terms of the charge carrier concentration rather than the charge carrier mobility. The electrical resistivity of the amorphous-IZO films deposited at R.T. was lower than that of the crystalline-IZO thin films deposited at 300°C . The change in the electrical resistivity with

increasing substrate temperature was interpreted mainly in terms of the charge carrier mobility rather than the charge carrier concentration. All the films showed a mean transmittance greater than 83% in the visible range. The optical band gap of the IZO films increased with decreasing O₂ flow rate. Furthermore, the optical band gap of the IZO films deposited at 300 °C was lower than that of the film deposited at room temperature at the same O₂ flow rate. The current density and luminance of the OLED devices with IZO thin films deposited at room temperature in 0.1sccm O₂ ambient gas were the highest among the films examined. These properties were attributed to the improved optical band gap, which plays a major role in the performance of OLED devices.

Acknowledgments

This study was supported partly by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0013509).

References

1. K. Ishibashi, K. Hirata, and N. Hosokawa, *Journal of Vacuum Science & Technology A*, 10 (1992) 1718-1722.
2. K. Tominaga, T. Ueda, T. Ao, M. Kataoka, and I. Mori, *Thin Solid Films* 281-282 (1996) 194-197.
3. Y. Hoshi, H. Kato, and K. Funatsu, *Thin Solid Films* 445 (2003) 245-250.
4. N. Taga, M. Maekawa, Y. Shigesato, I. Yasui, M. Kamei, and T. E. Haynes, *Jpn. J. Appl. Phys.* 37 (1998) 6524-6529.
5. C. Nunes de Carvalho, A. M. Botelho do Rego, A. Amaral, P. Brogueira, and G. Lavareda, *Surface and Coatings Technology* 124 (2000) 70 -75.
6. Y. S. Jung, J. Y. Seo, D. K. Lee, and D. Y. Jeon, *Thin Solid Films* 445 (2003) 63-71.
7. K. H. Noh, M. K. Choi, S. H. Park, and H. R. Joo, *Hankook Kwanghan Hoeji* 13 (2002) 455-459.
8. D. C. Paine, B. Yaglioglu, Z. Beiley, and S. Lee, *Thin Solid Films* 516 (2008) 5894-5898.
9. Y. S. Rim, H. J. Kim, and K. H. kim, *Thin Solid Films* 518 (2010) 6223-6227.
10. C. E. Kim, H. S. Shin, P. Moon, H. J. Kim, and I. Yun, *Current Applied Physics* 9 (2009) 1407-1410.
11. C. G. Choi, K. No, W. J. Lee, H. K. Kim, S. O. Jung, W. J. Lee, W. S. Kim, S. J. Kim, and C. Yoon, *Thin Solid Films* 258 (1995) 274-278.
12. R. Das, K. Adhikary, and S. Ray, *Appl. Surf. Sci.* 253 (2007) 6068-6073.
13. S. I. Jun, T. E. Mcknight, M. L. Simpson, and P. D. Rack, *Thin Solid Films* 476 (2005) 59-64.
14. D. Xu, Z. Deng, Y. Xu, J. Xiao, C. Liang, Z. Pei, and C. Sun, *Phys. Lett. A* 346 (2005) 148-152.
15. L. Raniero, I. Ferreira, A. Pimentel, A. Goncalves, P. Canhola, E. Fortunato, and R. Martins, *Thin Solid Films* 511-512 (2006) 295-298.
16. J. Tauc, R. Grigorovich, and A. Vancu, *Phys. Stat. Sol.* 15 (1966) 627-637.
17. J. Jia, A. Takasaki, N. Oka, and Y. Shigesato, *J. Appl. Phys.* 112 (2112) 013718-1-7.
18. D. H. Hwang, H. H. Ahn, K. N. Hui, K. S. Hui, and Y. G. Son, *J. Ceram. Proc. Res.* 12 (2011) 150-154.
19. D. H. Oh, Y. S. No, S. Y. Kim, W. J. Cho, J. Y. Kim, and T. W. Kim, *J. Ceram. Proc. Res.* 12 (2011) 488-491.