Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1089–1092
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Influence of annealing atmosphere on the structure, resistivity and transmittance of InZnO thin films

Chongmu Lee *, Wangwoo Lee, Hojin Kim, Hyoun Woo Kim

Department of Materials Science and Engineering, Inha University, 253 Yonghyeon-dong, Incheon 402-751, Republic of Korea

Abstract

Dependence of the electrical and optical properties of In_2O_3–10 wt% ZnO (IZO) thin films deposited on glass substrates by RF magnetron sputtering on the annealing atmosphere was investigated. The electrical resistivities of indium zinc oxide (IZO) thin films deposited on glass substrate can be effectively decreased by annealing in an $N_2 + 10\%\ H_2$ atmosphere. Higher temperature (200 °C) annealing is more effective in decreasing the electrical resistivity than lower temperature (100 °C) annealing. The lowest resistivity of $6.2 \times 10^{-4}\ \Omega$ cm was obtained by annealing at 200 °C in an $N_2 + 10\%\ H_2$ atmosphere. In contrast, the resistivity was increased by annealing in an oxygen atmosphere. The transmittance of IZO films is improved by annealing regardless of the annealing temperature.

Keywords: Optical properties; Electrical properties; ZnO; Transparent conducting oxide

1. Introduction

Indium tin oxide (ITO) which is most widely used as a transparent conducting oxide (TCO) electrode in flat panel displays (FPDs) and solar cells has low electrical resistivity ($\sim 2 \times 10^{-4}\ \Omega$ cm) as well as high transmittance (~90% at 550 nm). Nevertheless, ITO is an expensive TCO because indium in ITO is a rare and expensive element. Deterioration of the electrical and optical properties of ITO upon exposure to plasma is also known as its short-comings [1].

ITO thin films must be deposited at a temperature higher than 250 °C and then annealed at temperature higher than 300 °C for it to have high electrical conductivity and high transmittance [2]. This high temperature post-annealing makes the ITO films rough due to crystallization leading to significant deterioration of the device reliability. For this reason, there have been many efforts to replace ITO films by amorphous IZO (a-IZO) films in recent years. Besides the smoother surface, amorphous IZO has several advantages over ITO as follows: (1) a-IZO has higher structural stability at higher temperatures than ITO. The amorphous structure of IZO is maintained up to a temperature as high as 350 °C, which ensures good stability in both electrical and optical properties. (2) a-IZO has higher chemical stability than ITO. In particular for FPD applications, TCO films must be prepared at low temperatures below 200 °C to avoid thermal stress on the TFT devices or the flexible substrates. However, ITO films deposited at lower temperatures have lower resistance to moist heat, higher electrical resistivity, lower optical transmittance and poorer chemical stability. (3) a-IZO has the lowest resistivity when no reactive oxygen is added to the sputter chamber which simplifies the deposition process. (4) a-IZO has a lower internal stress which prevents exfoliation from the substrate during device fabrication processes. (5) a-IZO has better wet-etch performance [2–4].

Deposition of TCO films on glass substrates have been widely investigated during last decade. Recently, the necessity of studying deposition of TCO films on polymer substrates has increased because polymers substrates are suitable for flexible displays and electronics the demands of which are expected to increase explosively in the near future. Polymers have merits that they are cheaper and lighter than glass, but they also have several demerits. In comparison with glass substrates, polymer substrates have a lower thermal resistance, a weaker mechanical strength and a higher thermal expansion coefficient (20×10^{-6}/K [5]). The difference in thermal coefficient between polymer substrates and ZnO films (4.75×10^{-6}/K [6]) may result in residual thermal stress-induced defects. Other short-comings of polymers as substrate materials for TCO are

---

* Corresponding author. Tel.: +82 32 860 7536; fax: +82 32 862 5546.
E-mail address: cmlee@inha.ac.kr (C. Lee).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.09.053

that they easily absorb moisture and gas [7]. Therefore, it is necessary to use a buffer layer when TCO films are deposited on polymer substrates, which will make the polymer substrate surface smoother and reduce diffusion of vapor and oxygen. In this paper we report the effects of annealing temperature and atmosphere on the electrical resistance and optical transmittance of the IZO thin films prepare by radio frequency (RF) magnetron sputtering.

2. Experimental procedure

IZO thin films were deposited on PET substrates by RF magnetron sputtering using a 2 in. IZO (90 wt% In_2O_3–10 wt% ZnO). The maximum horizontal component magnetic field strength imposed on the target surface was 5×10^{-2} T. The PET surfaces were cleaned in an ultrasonic cleaner for 10 min with isopropyl alcohol and then blow dry with nitrogen before they were introducted into the sputtering system ZnO buffer layers were deposited using a 2 in. ZnO target. A ZnO buffer layer is expected to reduce the damage which would be done on the PET surface during deposition of the IZO film and to prevent chemical reactions with oxygen and moisture in the air and their diffusion into the PET substrate.

The deposition chamber were initially evacuated to 1×10^{-6} torr and oxygen and argon gas mixture was introduced into the chamber to maintain the desired pressure (1×10^{-3} torr). The Ar and O_2 gas flow rates were fixed at 20 and 10 sccm, respectively. The RF sputtering power and the substrate temperature were 80 W and room temperature, respectively. The IZO/ZnO/PET samples were annealed at 100 °C and 200 °C for 1 h in atmospheres of O_2, N_2 + 10% O_2, Ar + 10% H_2.

For the prepared samples, X-ray diffraction (XRD) analysis was performed to investigate the crystalline structure of the IZO films. An α-step (Dektak-3) was used to measure the film thicknesses. The carrier concentrations, carrier mobilities and electrical resistivities of the films were determined by using a Hall effect measurement system (HEM-2000). The optical transmittance was investigated by using a UV–VIS spectroscope.

3. Results and discussion

The carrier concentrations, carrier mobilities and resistivities of IZO/ZnO/PET samples at different annealing atmospheres and annealing temperatures are shown in Fig. 1. The resistivity of the IZO/ZnO/PET sample tends to be increased by annealing in an oxygen atmosphere regardless of annealing temperature. The elevation of resistivity seems to be mainly caused by a decrease in carrier concentration. As-deposited IZO films have a large number of oxygen vacancies and the number of oxygen vacancies is substantially reduced by annealing the IZO films in an O_2 atmosphere, resulting in a decrease in carrier concentration.

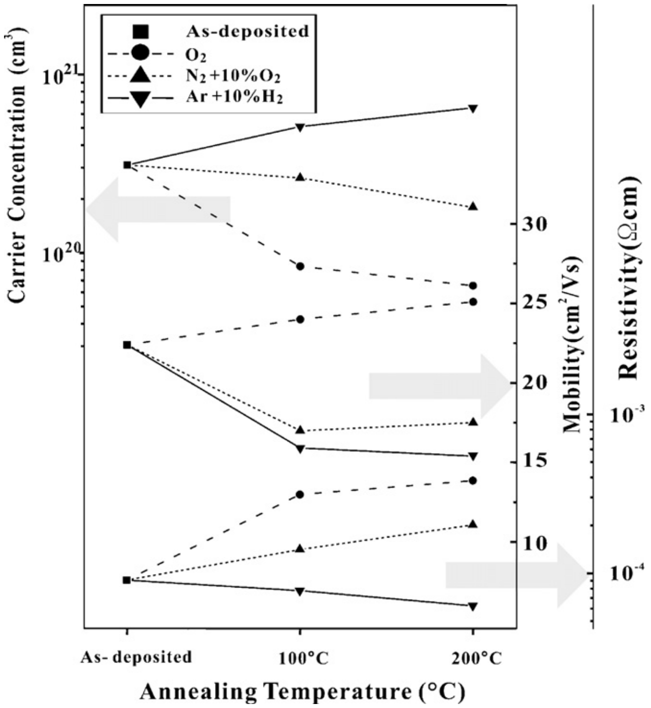

Fig. 1. The electrical properties of IZO thin films annealed at 100 and 200 °C in different atmospheres.

The resistivity of the IZO film is not nearly changed by annealing in an N_2 + 10% O_2 atmosphere. The carrier concentration seems to be decreased by annealing due to the same origin as explained above for O_2 annealing. However, the carrier mobility is increased by annealing in the N_2 + 10% O_2 atmosphere, which may be attributed to a decrease in the surface roughness and a slight increase in the particle size. It is well known that a smoother surface causes less surface scattering of charge carriers. The sputter deposited films usually consist of many small particles or nodules even if they had an amorphous structure. The particle size of the IZO film annealed in N_2 + 10% O_2 or Ar + 10% H_2 atmospheres is slightly larger than that of the as-deposited IZO film as shown in Fig. 2. The boundary between particles can be a barrier for carriers to move. A decrease in the boundary area between particles due to an increase in the particle size will result in an increase in the carrier mobility. The carrier concentration decreasing effect of annealing in an N_2 + 10% O_2 atmosphere seems to be compensated by its carrier mobility enhancing effect. As a result of this compensation no distinct change is noticed in the electrical resistivity by annealing in an N_2 + 10% O_2 atmosphere. In the case of N_2 + 10% H_2 annealing the carrier concentration has been decreased while the carrier mobility has been increased by annealing. As a result of the compensation of the carrier concentration decreasing effect and the carrier mobility increasing effect the resistivity has slightly decreased. The amorphous structure of the IZO film is maintained after annealing at 200 °C as shown in the XRD spectra in Fig. 3. However, as written above, the sputter-deposited films have interparticle boundaries even if they had an amorphous structure. Desorption of negatively charged oxygen species from the interparticle boundaries, which act as trapping sites and form potential barriers during annealing. The negatively charged species form depletion regions near the

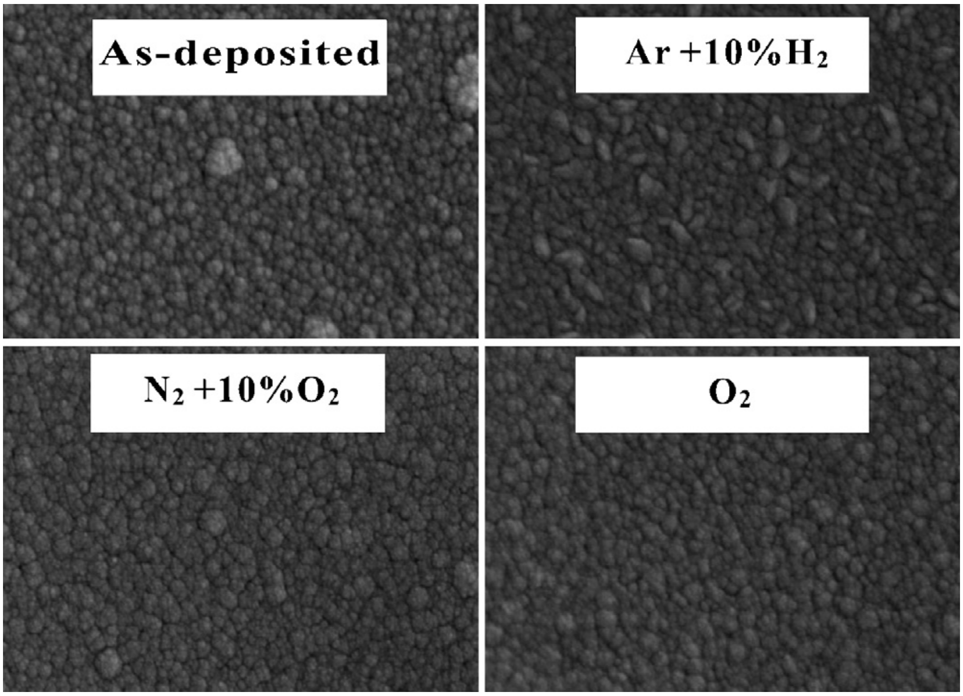

Fig. 2. SEM images of IZO thin films annealed at 200 °C in different atmospheres.

boundaries decreasing carrier concentration and mobility. Hydrogen atoms would passivate the boundary surface during the annealing treatment in an N_2 + 5% H_2 atmosphere and this hydrogen passivation would remove the depletion regions near the boundaries. The removal of the depletion region, in turn, would result in increases in carrier concentration and mobility.

Effects of annealing temperature on the electrical properties of IZO films are rather simple. Higher temperature (200 °C) annealing tends to change the resistivity more significantly than lower temperature (100 °C) annealing maybe because all the microstructural changes related to the resistivity are based on thermally activated processes.

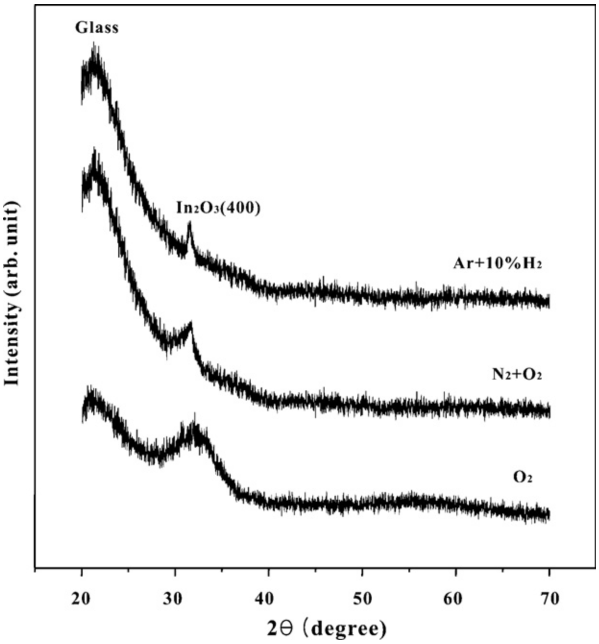

Fig. 3. X-ray diffraction spectra of IZO thin films at 200 °C.

Fig. 4 shows optical transmittance spectra of IZO thin films annealed in different atmospheres. All the annealed IZO thin films have the average transmittance >80%. It seems that the transmittance is improved by annealing regardless of the annealing atmosphere. This improvement in transmittance may be mainly attributed to a decrease in surface roughness with an increase in the annealing temperature. The wavelength of the absorption edge seems to strongly depend on the annealing atmosphere.

According to Burstein's report, the optical band gap increases with carrier concentration, which is known as B–M shift [8]. That is, the absorption edge shifts to the shorter wavelength region with carrier concentration. Our results in

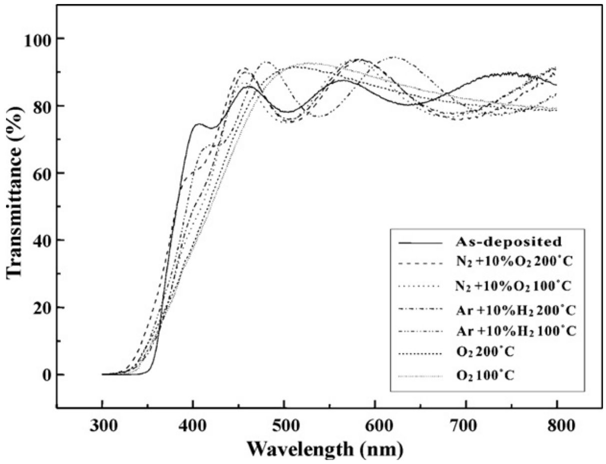

Fig. 4. Transmittance spectra of IZO/glass samples annealed at 100 and 200 °C in different atmospheres.

Fig. 4 show that annealing in an N_2 + 10% O_2 atmosphere shifts the absorption edge to a shorter wavelength, whereas annealing in an O_2 atmosphere shifts the absorption edge to a longer wavelength. As can be seen in Fig. 1, the carrier concentration has been increased by Ar + 10% H_2 annealing whereas it has been decreased by O_2 annealing. It may be said that our results regarding the shift of the absorption edge obeys the B–M shift. This result is consistent with our previous report on the Ga-doped ZnO that annealing in a reducing atmosphere widens the optical band gap, while annealing in an oxidizing atmosphere makes the optical band gap narrower [9].

4. Conclusions

The electrical resistivities of indium zinc oxide (IZO) thin films deposited on glass substrate can be effectively decreased by annealing in an N_2 + 10% H_2 atmosphere. Higher temperature (200 °C) annealing is more effective in decreasing the electrical resistivity than lower temperature (100 °C) annealing. The lowest resistivity of $6.2 \times 10^{-4}\ \Omega\,\mathrm{cm}$ was obtained by annealing at 200 °C in an N_2 + 10% H_2 atmosphere. In contrast, the resistivity was increased by annealing in an oxygen atmosphere. The transmittance of IZO films is improved by annealing regardless of the annealing atmosphere.

Acknowledgement

This work was supported by Inha University.

References

[1] H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, Semiconduction Transparent Thin Films, Institute of Physics Publishing, Bristol and Philadelphia, 1995.

[2] B. Yaglioglu, Y.-J. Huang, H.-Y. Yeon, D.C. Paine, A study of amorphous and crystalline phases in In_2O_3–10 wt% ZnO thin films deposited by DC magnetron sputtering, Thin Solid Films 496 (2006) 89–94.

[3] J.-T. Ho, C.-Y. Chen, Power effects in indium–zinc oxide thin films for OLEDs on flexible applications, J. Electrochem. Soc. 152 (2005) G57–G61.

[4] B. Yaglioglu, H.-Y. Yeom, D.C. Paine, Crystallization of amorphous In_2O_3–10 wt% ZnO thin films annealed in air, Appl. Phys. Lett. 86 (2005) 261908.

[5] Dupont Tejjin Films: 'Kaladex 1020', Technical date sheet KXTD 005-K 1020, Dupont Teijin Films, Wilton, UK.

[6] K. Ellmer, Magnetron sputtering of transparent conductive zinc oxide: relation between the sputtering parameters and the electronic properties, J. Phys. D: Appl. Phys. 33 (2000) R17–R32.

[7] M. Fahland, P. Karlsson, C. Charton, Low resisitivity transparent electrodes for displays on polymer substrates, Thin Solid Films 392 (2001) 334–337.

[8] Z.C. Jin, I. Hamberg, C.G. Granqvist, Optical properties of sputter-deposited ZnO:Al thin films, J. Appl. Phys. 64 (1988) 5117–5131.

[9] S. Kim, W. Lee, C. Lee, Influence of ZnO buffer layer thickness on electrical and optical properties of GZO thin films deposited on polymer substrates, Mater. Sci. Technol. 23 (2007) 303–306.