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Fabrication of IZO thin films for flexible organic light emitting diodes by RF magnetron sputtering

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We have investigated the effect of ambient gases on the structural, electrical, and optical characteristics of IZO thin films intended for use as anode contacts in the organic light emitting diodes (OLED) devices. These IZO thin films were deposited on the PES film by radio frequency (RF) magnetron sputtering under different ambient gases (Ar, Ar + O_2, and Ar + H_2) at room temperature. In order to investigate the influences of the ambient gases, the flow rate of oxygen and hydrogen in argon has been changed from 0.1 sccm to 0.5 sccm, respectively. All the IZO thin film has an (222) preferential orientation regardless of ambient gases. The electrical resistivity of the IZO film increased with increasing O_2 flow rate, whereas the electrical resistivity decreased sharply under an Ar + H_2 atmosphere and was nearly similar regardless of the H_2 flow rate. The change of electrical resistivity with changes in the ambient gas composition was mainly interpreted in terms of the charge carrier concentration rather than the charge carrier mobility. All the films showed the average transmittance over 85% in the visible range. The OLED device was fabricated with different IZO substrates made with the configuration of IZO/α-NPD/DPVB/Alq_3/LiF/Al in order to elucidate the performance of the IZO substrate. The current density and the luminance of OLED devices with IZO thin films deposited in 0.5 sccm H_2 ambient gas are the highest amongst all other films.

Key words: IZO thin film, RF magnetron sputtering, Ambient gas, Electrical resistivity, OLED device.

Introduction

Transparent conducting oxide (TCO) thin films have been extensively studied, especially for their applications to display devices such as liquid crystal display (LCD), plasma display panel (PDP) and organic light emitting diodes (OLED)[1-3]. Of all the TCO films, ITO thin films have been extensively utilized in these devices because of their high transmittance in the visible range and low electrical resistivity [4, 5]. However, in order to have high electrical conductivity and high transmittance, ITO thin films must be deposited and then annealed at temperature higher than 250 °C and 300 °C, respectively. This high temperature post-annealing makes the ITO films rough due to the crystallization, which leads to significant deterioration of the device reliability [4, 5].

Recently, new transparent conducting oxide such as indium zinc oxide (IZO) thin films has emerged as promising anode materials for OLEDs due to their low deposition temperature, high work function, low resistivity, excellent chemical stability, and high transmittance over 90% in the visible spectrum range [6-8]. IZO thin films can be deposited by RF magnetron sputtering technique which has been widely used due to 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 the 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]. The effect of oxygen in the reactive sputtering on the electrical and structural properties of TCO films has been studied by several groups [9, 10]. The roles of the partial pressure of oxygen and hydrogen on the structural as well as the optical and electrical properties of RF magnetron sputtered TCO films were also discussed [11]. These research works have concluded that the electrical resistivity correlates strongly with the stoichiometry of the IZO thin films. Considering these facts, it is interesting to study the effect of the ambient gas on the structure and the electrical resistivity, and especially on the charge carrier concentration and charge carrier mobility of the IZO thin films. Furthermore, in this study we have investigated the effect of the structure and electrical resistivity of IZO thin films on the performance of OLED devices. For this purpose, Zn-doped In_2O_3 (IZO) films were deposited by RF magnetron sputtering under various ambient gases (Ar, Ar + O_2, and Ar + H_2). The electrical resistivity and the surface morphology of the TCO thin films were systematically examined. In order to elucidate the effect of the electrical resistivity on the performance of OLED devices, the organic materials and cathode electrode were sequentially deposited on the TCO thin films. Then, the electrical characteristics such as current density vs. voltage and luminescence vs. voltage of OLED devices were measured.

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Experimental

The IZO thin films were prepared by RF magnetron sputtering with a mixture of a 90% indium oxide and 10% zinc oxide target. The PES substrates (i-component) were firstly cleaned with standard cleaning procedures and then rinsed in deionized water. The sputtering chamber was evacuated by a turbomolecular pump to the base pressure of about 1.33×10^{-4} Pa. In order to investigate the influences of the oxygen and hydrogen, the flow rate of oxygen and hydrogen in the argon mixing gas has been changed from 0.1 to 0.5 sccm. The sputtering gas was Ar and the substrate temperature was room temperature. Table 1 indicates the experimental conditions for the deposition of IZO thin films.

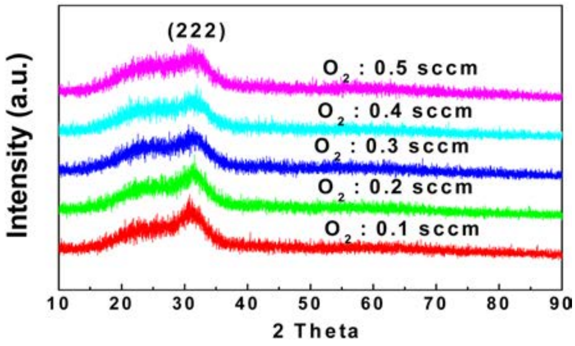
The microstructural observation and crystal orientation of the IZO thin films were evaluated by using X-ray diffraction (Rigaku, RTP300RC) and field emission scanning electron microscope (Jeol, JSM7500F), respectively. The optical transmittance of IZO thin films was measured using an ultraviolet spectrophotometer (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 a hall effect measurement (HMS-3000, ECOPIA, KOR). Then, the organic materials and cathode electrode were sequentially deposited on the TCO thin films. The device structure was IZO/α-NPD(N, N-Di(naphthalene-1-yl)-N, N'-diphenyl-benzidine)/DPVB ((diphenylvinyl) benzene)/Alq_3/LiF/Al. The 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 by using a spectrometer (CS-1000A, Konica Minolta Sensing Int, Japan).

Results and discussion

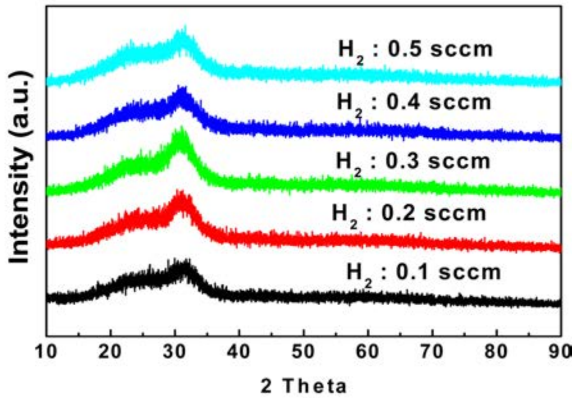
The XRD patterns of the IZO thin films deposited using RF magnetron sputtering are presented in Fig. 1. It is clearly seen that the IZO phase is fully stabilized (within a detection limit of XRD) and a small broad

Table 1. Conditions of sputtering IZO thin films.

Deposition parameters	Conditions
Target	In_2O_3/ZnO(90/10 wt.%)
Target diameter (inch)	3
Substrate	PES(i-component)
Working pressure (Pa)	7.98×10^{-1}
Film thickness (nm)	300
Substrate temperature	Room temperature
RF power (W)	80
Gas ambient (sccm)	Ar:40, O_2 flow rate : 0.1-0.5, H_2 flow rate : 0.1-0.5



(a)



(b)

Fig. 1. XRD patterns of the IZO thin films deposited in (a) O_2 and (b) H_2 ambient gases.

In_2O_3 (222) peak at 30.54 ° is the most prominent peaks indicating that the IZO film has an (111) preferential orientation. Furthermore, with the increase of oxygen and hydrogen concentration, the intensity of (222) peak remains unaltered. It has been reported that a specific preferred orientation of thin film can be discussed on the basis of strain and surface energies [12]. At thin film thicknesses the surface energy controls growth and at thick film thicknesses the strain energy predominates. Based on the above discussions, it can be concluded that the (111) plane of IZO thin films has the lowest strain.

Microstructural features of the IZO thin films with different ambient gases are presented in Fig. 2. There is not any second phase observed. The grain sizes in IZO thin films are nearly similar regardless of ambient gases. However, it is very interesting to note that with the increase of oxygen and hydrogen concentration, small cracks are observed among the grains and the amount of hazy phases decreases, indicating that the film surface could be etched off by oxygen and hydrogen bombardment through the physical interaction [13]. From the results of Figs.1 and 2, it seems that the ambient gases have an important effect upon the physical characteristics such as crystal orientation and microstructure of thin films.

Since the surface properties of the TCO thin films for anode materials may affect the characteristics of the OLED devices [14], it is very important to investigate the

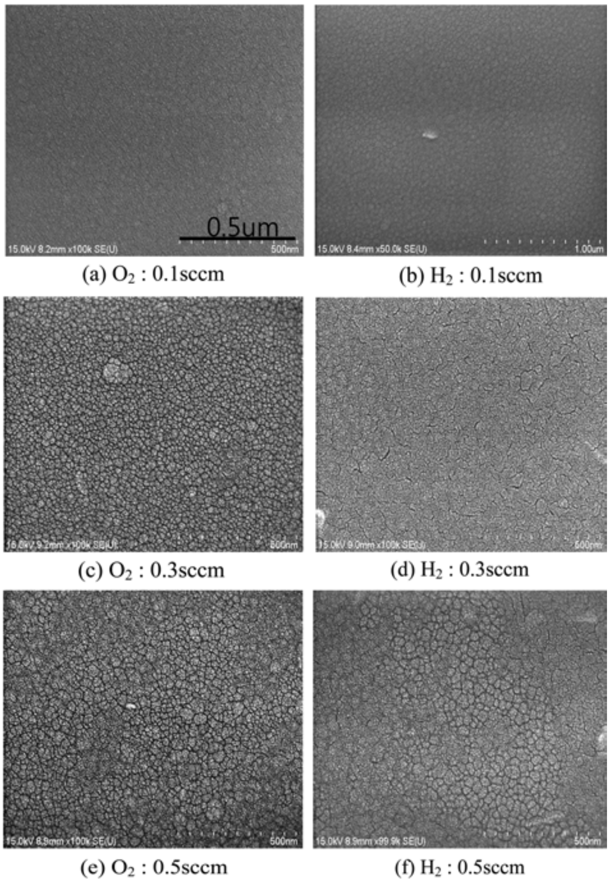


Fig. 2. FE-SEM micrographs of IZO thin films with different ambient gases.

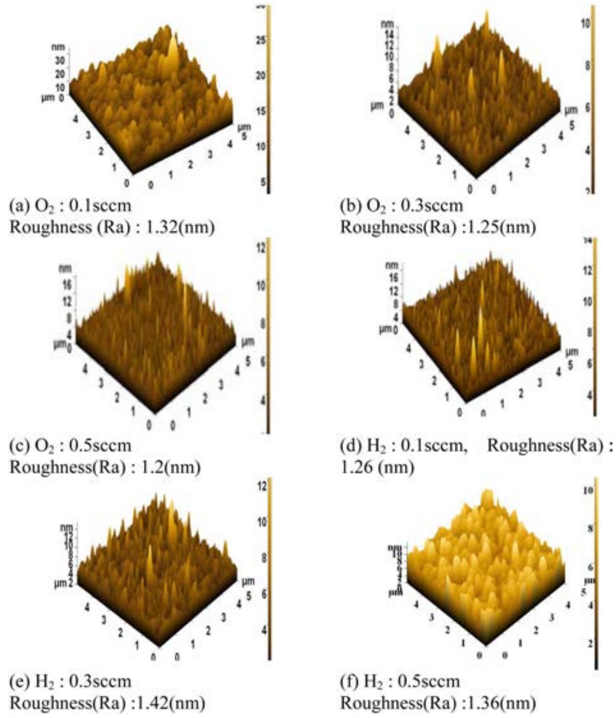
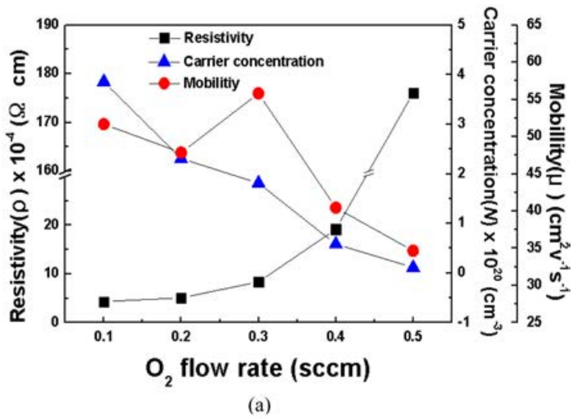


Fig. 3. AFM morphologies of the IZO films deposited with different ambient gases.



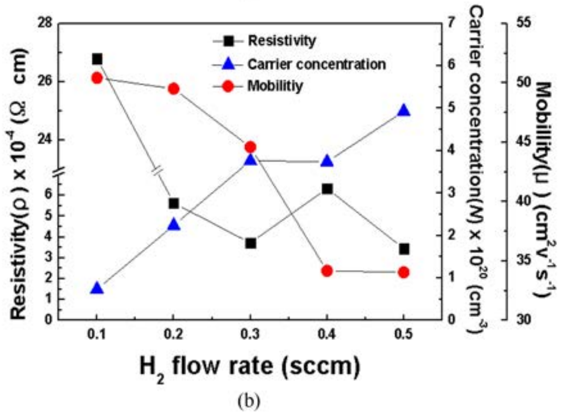


Fig. 4. Resistivity (ρ), mobility (μ) and carrier concentration (*N*) of IZO thin films with flow rate of (a) O_2 and (b) H_2 with Ar.

surface morphology of the IZO thin films. Fig. 3 presents the AFM images of IZO thin films deposited under the various ambient gases. All surfaces are very flat and no very sharp peak appears in the domain. Furthermore, it seems that the surface roughness is not directly related to the concentration and kind of ambient gas.

Fig. 4 presents the electrical resistivity (ρ), charge mobility (μ), and charge carrier concentration (*N*) of the IZO thin films with flow rates of (a) O_2 and (b) H_2. The resistivity of the IZO films increases with increasing O_2 flow rate, which is attributed to the decrease of the charge carrier mobility and charge carrier concentration. The electrical resistivity decreases very sharply under an Ar + H_2 atmosphere and is nearly similar regardless of the H_2 flow rate. This can be interpreted in terms of the drastic increase of the charge carrier concentration. It is now well established that oxygen vacancies in In_2O_3 based TCO thin film act as donors and their presence make the film less resistive [11]. During reactive sputtering under ambient oxygen the thin film becomes more stoichiometric and the concentration of oxygen vacancies decreases. Thus, the electrical resistivity increases. Under reactive sputtering with hydrogen, due to the reducing property of hydrogen, oxygen vacancies are created in IZO thin films. Therefore, the resistivity of such films deposited under Ar + H_2 gas ambient is much lower compared to that of the film deposited under Ar + O_2.

Fig. 5 presents the optical property of the IZO films

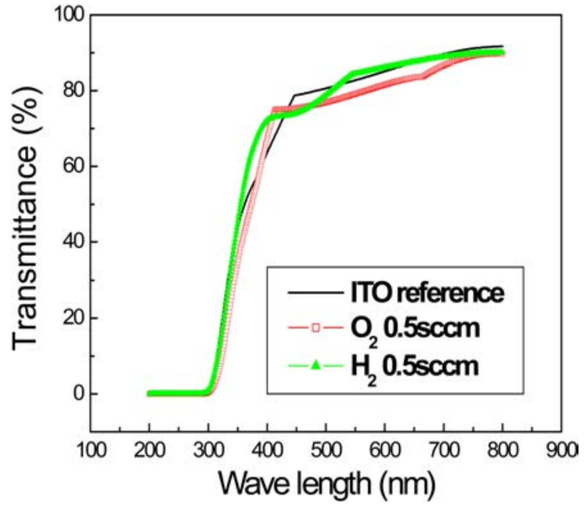


Fig. 5. Optical transmittance spectra of IZO thin films with different ambient gases.

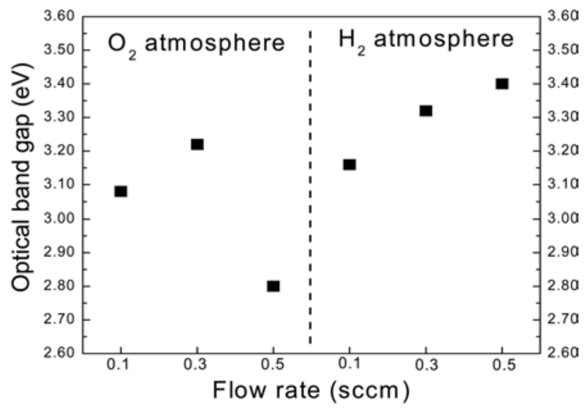


Fig. 6. Optical band gap of IZO thin films with flow rate of O_2 and H_2 with Ar.

with different ambient gases. It is seen that the average transmittance in the visible wavelength region is over 85% for all the IZO thin films. The increase in transmittance over a wider wavelength range may be beneficial for certain applications of TCO thin films, e.g. as a window layer in thin film solar cells.

The $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) is plotted to determine the band gap energy of the IZO thin films. The optical band gap energies of the IZO films, as determined from the obtained transmittance spectra, are shown in Fig. 6. The optical band gap of the IZO films increases with increasing H_2 flow rate. However, it seems that the optical band gap of the IZO films deposited under O_2 atmosphere is not directly related to the concentration of ambient gas. It has been reported that an increase in the Fermi level in the conduction band of degenerate semiconductors leads to a band gap widening effect, which is consistent with our experimental results.

Fig. 7 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 is IZO/α-NPD/DPVB/Alq_3/LiF/Al. The DPVB is used as

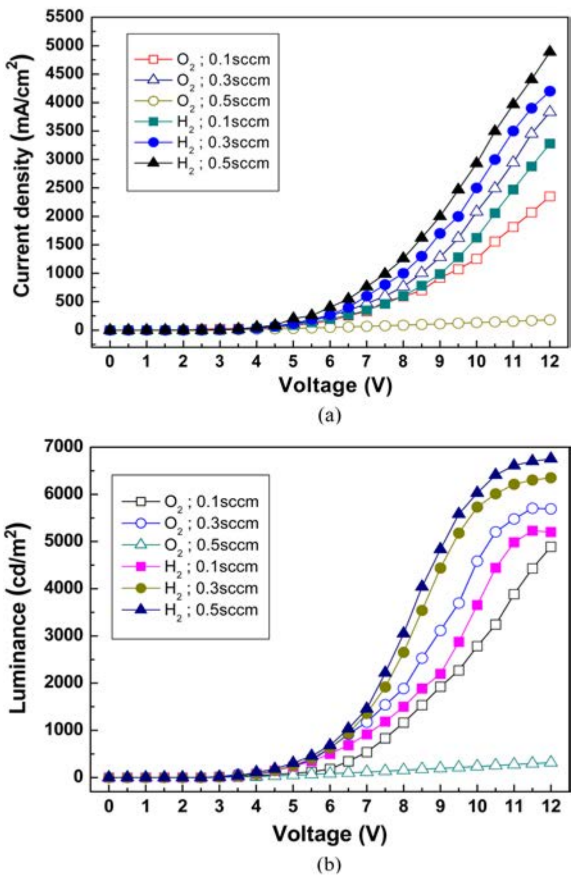


Fig. 7. (a) I-V and (b) L-V characteristics of the OLED Devices.

a blue emitting material. As shown in Fig. 7, the current density and the luminance of OLED devices show higher value with the following order : $O_{0.5\ sccm} < O_{0.1\ sccm} < H_{0.1\ sccm} < O_{0.3\ sccm} < H_{0.3\ sccm} < H_{0.5\ sccm}$. This order is perfectly consistent with that of value of optical band gap energies of the IZO films with different ambient gases (Fig. 6). If the electrical resistivity is considered as the main parameter affecting the current density and the luminance, the current density and the luminance should show value by the following order : $O_{0.5\ sccm} < H_{0.1\ sccm} < O_{0.3\ sccm} < O_{0.1\ sccm} < H_{0.3\ sccm} < H_{0.5\ sccm}$. Therefore, the results of Fig. 7 clearly indicates that hole injecting ability of the IZO anode is largely dependent on the optical band gap energies of IZO thin films. As shown in Fig. 7, the current density and the luminance of OLED devices with IZO thin films deposited in 0.5 sccm H_2 ambient gas are the highest amongst all other films considered. From the results of Figs. 7 and 6, it can be clearly concluded that the optical band gap energy of IZO thin films plays a major role in OLED device performance, especially the current density and luminance.

Conclusions

Structural, electrical, and optical properties of the IZO thin films were systematically examined for use as the anode contact in OLED device. IZO thin films were deposited by RF magnetron sputtering under the different ambient gases (Ar, $Ar + O_2$, and $Ar + H_2$) at room temperature. All the IZO thin film has an (222) preferential orientation regardless of ambient gases. The electrical resistivity of IZO thin films increases with increasing O_2 flow rate, and dramatically decreases under $Ar+H_2$ atmosphere. It is important to note that the electrical resistivity of IZO thin films is mainly associated with the charge carrier concentration. All the IZO thin films have a high transmittance regardless of ambient gases. The optical band gap energy of IZO thin films plays a major role in OLED device performance, especially the current density and luminance

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