Electrochemical and Solid-State Letters, **10** (6) J75-J78 (2007)
1099-0062/2007/10(6)/J75/4/$20.00 © The Electrochemical Society

High-Performance Flexible Organic Light-Emitting Diodes Using Amorphous Indium Zinc Oxide Anode

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We demonstrate a high-performance flexible organic light-emitting diode (OLED) employing amorphous indium zinc oxide (IZO) anode. The amorphous IZO on flexible polycarbonate (PC) substrate shows similar electrical conductivity and optical transmittance with commercial (ITO) glass, even though it was prepared at $<50°C$. Moreover, it exhibits little resistance change during 5000 bending cycles, demonstrating good mechanical robustness. A green phosphorescent OLED fabricated on amorphous IZO on flexible PC shows maximum external quantum efficiency of $\eta_{ext} = 13.7\%$ and power efficiency of $\eta_p = 32.7$ lm/W, which are higher than a device fabricated on a commercial ITO on glass ($\eta_{ext} = 12.4\%$ and $\eta_p = 30.1$ lm/W) and ITO on flexible PC ($\eta_{ext} = 8.5\%$ and $\eta_p = 14.1$ lm/W). The mechanical robustness and low-temperature deposition of IZO combined with high OLED performance clearly manifest that the amorphous IZO is a promising anode material for flexible displays.
 [DOI: 10.1149/1.2720635]

Manuscript submitted October 3, 2006; revised manuscript received February 12, 2007. Available electronically March 30, 2007.

There has been increasing activity for flexible organic light-emitting diodes (OLEDs) over the past few years, and it has focused on developing indium tin oxide (ITO)-coated polymer substrates, such as polyethylene terephthalate (PET),[1-5] polycarbonate (PC),[6,7] polyimide,[8] polyethersulfone (PES),[9] polyethylene naphthalate (PEN),[9] and polycyclic olefin (PCO).[9] However, ITO electrode comes with its own set of problems such as chemical instability in a reduced ambient, poor transparency in the blue region, release of oxygen and indium into the organic layer, imperfect work function alignment with typical hole-transport layers, and easy deterioration of ITO targets.[5] In addition, the optimum properties of ITO film can only be obtained from fully crystallized film deposited at high temperature ($\sim 300°C$) or annealed in air or oxygen ambient.[10] With the increasing interest in the development of flexible OLEDs, there is great need for a more mechanically robust and transparent electrode because the resistance of crystallized ITO films on flexible substrate increases with increasing mechanical stain. The increase in resistance is related to the number of cracks generated in the electrode, which depends on applied strain and film thickness.[1,3]

For this reason, new transparent conducting materials have been explored to replace ITO for flexible OLED anodes. To achieve better performance of flexible OLEDs, Zn-based transparent conducting oxide (TCO) films, such as $ZnSn_2O_4$, $ZnSnO_3$, $Zn_2In_2O_5$, and Al(Ga)-doped ZnO, have been applied as the anode.[11-16] Among various Zn-based transparent conducting oxides, the Zn-doped In_2O_3 (IZO) films recently have been recognized as promising TCO materials for OLEDs due to its good conductivity, high transparency, excellent surface smoothness, high etching rate, and low deposition temperature.[13-16] In particular, it has been confirmed that electrical and optical properties of amorphous IZO (a-IZO) films can be optimized at $<50°C$ without a postannealing process. Therefore it is considered that a-IZO anode films can be applied to flexible displays, acquiring low temperature process, high conductivity, high transparency, and high mechanical robustness.[14-17] Even though a-IZO has been reported as a candidate material for flexible OLEDs, there are few reports on flexible OLEDs using a-IZO as the anode, and they showed rather poor performance with external quantum efficiency of less than 0.5% using Alq_3 as the emitter.[11,14,17]

In this article, we report high-performance, flexible OLEDs using an a-IZO anode grown by dc magnetron reactive sputtering at the temperature of $<50°C$ on a PC substrate. It was found that the a-IZO anode films deposited at $<50°C$ have similar conductivity, transparency, and surface smoothness as a commercial crystalline ITO (c-ITO) anode on glass prepared at high temperature ($\sim 300°C$). Furthermore, the OLEDs fabricated using the a-IZO anode on the flexible substrate exhibit similar or slightly superior device performance and efficiency to a device fabricated on c-ITO anode on glass. In the flexibility test, the a-IZO on a flexible substrate showed very small resistance change during 5000 bending cycles, demonstrating good mechanical robustness.

The IZO and ITO films were deposited on the polymer substrate of PC by a dc magnetron reactive sputtering system using a sintered indium zinc oxide target (In_2O_3:ZnO = 90:10 wt %) and indium tin oxide target (In_2O_3:SnO_2 = 90:10 wt %), respectively. The PC substrate (Glastic PC) has a glass transition temperature of $\sim 150°C$ and a coefficient of thermal expansion of 50–60 ppm/°C. The sputtering was carried out at a pressure of 4×10^{-1} Pa with a sputtering power of 1000 W. Argon mixed with oxygen was used as the reactive sputtering gas with the mixing ratio of $O_2/Ar = 0.04$ and $O_2/Ar = 0.01$ for a-IZO and ITO films, respectively. The substrate temperature was maintained lower than 50°C. The work function of a-IZO anode and ITO anode films were measured by a photoelectron spectroscopy with a UV source (PKI model AC-2) at atmospheric pressure after UV-ozone treatment.

The microstructures of the c-ITO anode (Asahiglass Fine Techno Co., Ltd.), and IZO and ITO films deposited at $<50°C$ were characterized by X-ray diffraction (XRD) measurement as shown in Fig. 1. The XRD pattern of the c-ITO anode film exhibited crystalline structure as expected with the peaks at $2\theta = 30.1°$ (222), 35.20° (400), 50.44° (440), and 60.22° (622) in Fig. 1a. The XRD patterns of the IZO[18] and ITO anode film deposited at $<50°C$ show a weak and broad peak characteristic of amorphous structure (Fig. 1b and c).

Figure 2 shows the optical transmittance spectra of the a-IZO and ITO films deposited on the PC and glass substrate. The optical transmission of the 150 nm thick a-IZO film deposited at $<50°C$ is almost the same as the c-ITO on glass film in the visible range (450–700 nm) except the deep blue region (400–450 nm). The average transmission was about 81% including PC substrate, which is almost the same as the previous reported result.[15] The optical transmittance of the 150 nm thick a-ITO on PC substrate is much lower than the a-IZO, especially in the wavelength range of 500–700 nm with the average transmittance of 77%. To obtain transparent c-ITO

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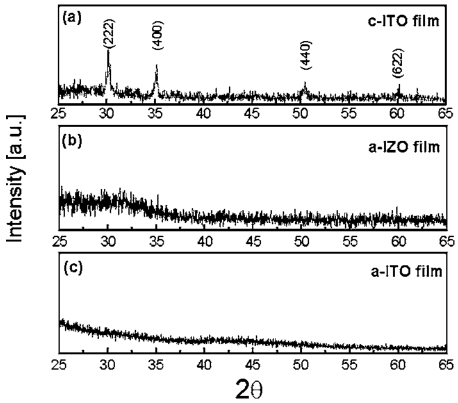

Figure 1. (Color online) Comparison of XRD patterns obtained from (a) c-ITO, (b) a-IZO, and (c) a-ITO anode films.

anode films, they are usually grown at high temperature (~300°C) with oxygen gas flow. However, the a-IZO films with high transmittance can be obtained at <50°C, which is desirable for flexible displays on plastic substrates.

Table I summarizes the electrical and optical properties of the films for comparison. The sheet resistance of the a-IZO/PC (~30 Ω/□) is much lower than a-ITO/PC (~60 Ω/□) but higher than c-ITO/glass (~10 Ω/□), which is similar to the recently reported results.[15] Despite the higher resistance of the a-IZO anode than c-ITO, the electrical conductivity is good enough for high-performance OLEDs, which is demonstrated from the OLED performance described below.

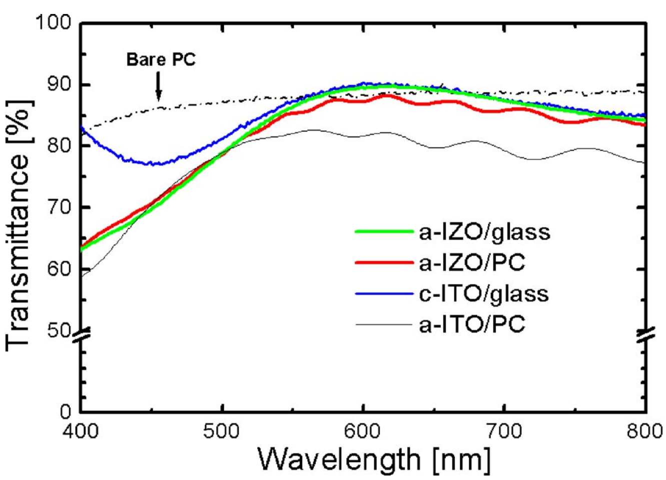

Figure 2. (Color online) Optical transmittance spectra of a-IZO/PC and a-IZO/glass film. For comparison, the transmittance of bare PC substrate, a-ITO/PC, and c-ITO/glass are also shown.

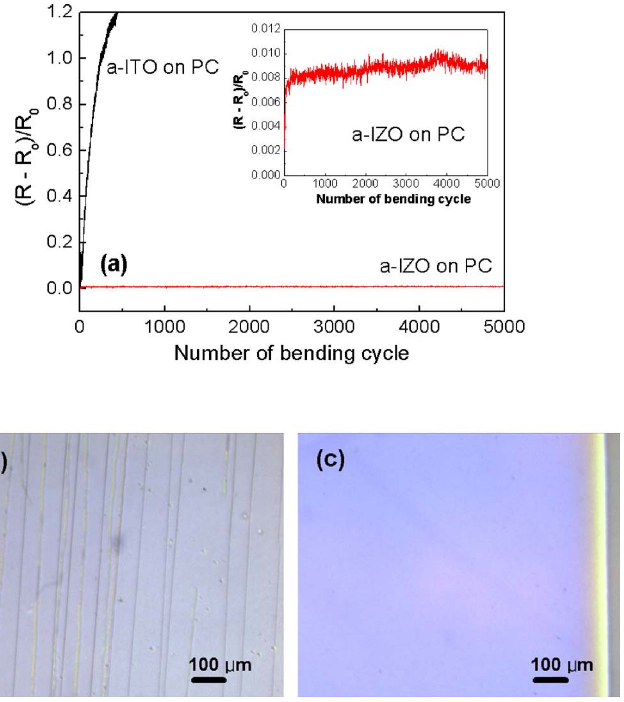

Figure 3. (Color online) (a) Normalized resistance change after repeated bending as a function of the number of cycles for a-ITO/PC and a-IZO/PC substrate and optical micrographs of (b) a-ITO/PC and (c) a-IZO/PC after bending test.

To investigate the flexibility of the transparent electrodes prepared on the 100 µm thick PC substrate, we have devised a laboratory-made bending test system. The a-ITO/PC and a-IZO/PC substrate with 100 mm length and 15 mm width were clamped in a semicircle two parallel plates. One plate was mounted to the shaft of a motor, while the other was fixed to a rigid support. The distance of stretched mode was 80 mm and that of bended position was 30 mm, i.e., the stroke of bending test was 50 mm. The bending radius was approximated to 8 mm and the bending frequency was 1 Hz. During the bending test, the resistance of the samples was measured by a multimeter through the conductive clamps. The change in resistance is shown in Fig. 3a, where R_0 is the initial resistance and R is the measured resistance after bending. The resistance of the a-ITO film deposited on PC at <50°C increases drastically at initial bending operation because of the generation and propagation of cracks (Fig. 3b).[1-3] However, the a-IZO film shows very small increase of resis-

Table I. Summary of the electrical/optical properties, and device performances on c-ITO/glass, a-ITO/PC a-IZO/glass, and a-IZO/PC substrates.

Anode materials	Sheet resistance (Ω/□)	Average transmission (400–700 nm) (%)	Work function (After O_3 treatment) (eV)	Max. EQE (%)	Max. PE (lm/W)	EQE (at 10 mA/cm^2) (%)	PE (at 10 mA/cm^2) (lm/W)
c-ITO/glass (Commercial ITO)	~10	~84	~5.0	12.4	30.1	8.1	8.8
a-ITO/PC (Grown at <50°C)	~60	~77	~5.0	8.5	14.1	8.0	9.0
a-IZO/glass (Grown at <50°C)	~30	~82	~5.2	13.2	30.7	8.6	9.4
a-IZO/PC (Grown at <50°C)	~30	~81	~5.2	13.7	32.7	8.5	9.8

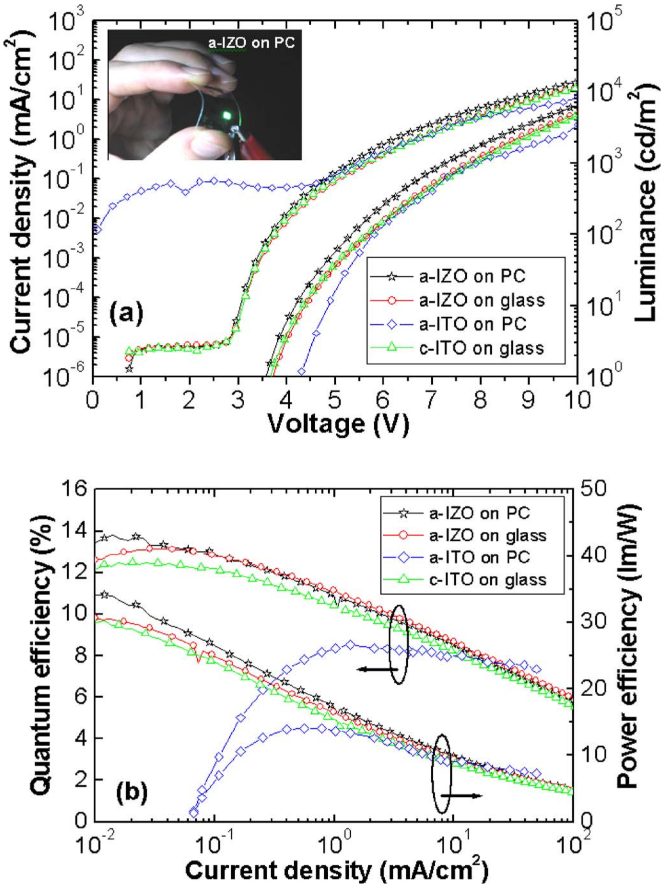

Figure 4. (Color online) (a) *J-V* and *L-V* characteristics, and (b) external quantum efficiency and power efficiency vs current density for a-IZO/PC, a-IZO/glass, a-ITO/PC, and c-ITO/glass-based device. The inset shows the photograph of the flexible OLED fabricated on a-IZO/PC substrate after bending.

tance during the 5000 bending cycles without generation of cracks (Fig. 3c). Thus, the a-IZO film prepared in this work is much more ductile than the a-ITO film. The robustness combined with the good electrical conductivity and high optical transparency of the a-IZO films deposited at $<50°C$ demonstrates its potential as high-performance anodes for the flexible devices.

Phosphorescent OLEDs were fabricated on a-IZO/glass, a-IZO/PC, c-ITO/glass, and a-ITO/PC substrates for comparison. Prior to organic layer deposition, the substrates were exposed to UV-ozone flux for 10 min following degreasing in aceton and IPA. All organic layers were grown by thermal evaporation at the base pressure of $<5 \times 10^{-8}$ Torr in the following order: hole transporting layer (HTL)/emission layer (EML)/hole blocking layer (HBL)/electron transporting layer (ETL)/cathode. A 40 nm thick 4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB) was used as the HTL, 30 nm thick a *N*,*N*'-dicarbazolyl-4-4'-biphenyl (CBP) doped with 6 wt % $Ir(ppy)_3$ as the EML, 10 nm thick 2,9-dimethyl-4,7-diphenyl-1.10-phenanthroline (BCP) as the HBL and 40 nm thick tris-(8-hydroxyquinoline) aluminum (Alq_3) as the ETL, respectively. The cathode consisting of a 1 nm thick LiF and a 100 nm thick layer of Al was deposited through 1 mm diameter openings in a shadow mask placed onto the sample surface. Current density-voltage-luminescence (*J-V-L*) characteristics of OLED were measured simultaneously using a Keithley 2400 programmable source meter and a Newport 1835C optical meter equipped with a Newport 818-UV silicon photodiode. The setup is calibrated by comparison with direct luminance measurements using a SpectraScan PR650 (Photo Research).

Figure 4 exhibits the *J-V-L* characteristics of the phosphorescent OLEDs fabricated on the a-IZO/PC, a-IZO/glass, a-ITO/PC, and the c-ITO/glass substrates. In spite of higher sheet resistance of the a-IZO anode than the c-ITO anode, the *J-V* curve of a-IZO based device shows slightly higher current density and lower turn-on voltage than that of c-ITO (Fig. 4a). In addition, both devices exhibit very low leakage current density before the turn-on voltage due to absence of a shunt resistance, which is indicative of leaky interfaces between anode/organic and cathode/organic interfaces. However, the OLED fabricated on the a-ITO/PC substrate exhibit very large leakage current density before turn-on voltage, and higher turn-on voltage than the a-IZO and c-/ITO anodes. It is noteworthy that the external quantum efficiency (EQE) and power efficiency (PE) of the a-IZO-based device are higher than those of c-ITO and a-ITO, as shown in Fig. 4b and summarized in Table I. A maximum EQE of 12.4% and PE of 30.1 lm/W are obtained for the c-ITO/glass-based device, similar to the recently reported results.[19,20] The a-IZO/PC and a-IZO/glass-based devices result in almost the same device performance with the maximum EQE of 13.7% and the PE of 32.7 lm/W, and EQE of 13.2% and PE of 30.7 lm/W, respectively. Furthermore, the bended device of a-IZO/PC emits bright green light clearly visible under ordinary room light, as shown in the inset of Fig. 4a. The a-ITO/PC-based device exhibits much poorer device performance (EQE = 8.5%, PE = 14.1 lm/W) than a-IZO/PC, which may come from the large leakage current in the device.

The higher work function of the a-IZO anode ($\sim$5.2 eV) than that of c-ITO ($\sim$5.0 eV) leads to more efficient hole injection in OLEDs by reducing the barrier height between anode and HTL. Although the grown a-IZO anode shows a higher sheet resistance than that of a c-ITO anode, the high hole injection efficiency of the a-IZO anode due to high work function may lead to lower turn-on voltage than that of c-ITO and a-ITO, resulting in high EQE and PE.

In summary, we have demonstrated a high-performance flexible OLED using a-IZO anode. The a-IZO on a flexible PC substrate showed high electrical conductivity and optical transmittance comparable with c-ITO on glass, and very good mechanical robustness upon bending, even though it was prepared at $<50°C$. The a-IZO devices showed better external quantum efficiency and power efficiency than the device on c-ITO/glass and a-ITO/PC. All the characteristics clearly demonstrate that the a-IZO is a promising transparent anode material, replacing c-ITO and a-ITO for flexible displays.

Acknowledgments

This work was supported by the Ministry of Commerce, Industry, and Energy through the OLED center and Samsung SDI. H.K.K. thanks the Korea Research Foundation (contract no. KRF-2006-331-D00243) for its support.

Seoul National University assisted in meeting the publication costs of this article.

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