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 \( <50^\circ\text{C} \). 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 \( \eta_{\text{ex}} = 13.7\% \) and power efficiency of \( \eta_p = 32.7 \text{ lm/W} \), which are almost the same as the previous reported result.\(^{15}\) The optical transmittance of PC by a dc magnetron reactive sputtering system using a sintered In2O3:SnO2 = 90:10 wt % target was 77\%. To obtain transparent c-ITO, the work function of IZO film was characterized by X-ray diffraction measurement as shown in Fig. 1a. The XRD pattern of the c-ITO anode film exhibited crystalline structure as expected with the peaks at \( 2\theta = 30.1^\circ \) (222), 35.20° (400), 50.44° (440), and 60.22° (622) in Fig. 1a. The XRD patterns of the IZO and ITO anode film deposited at \( <50^\circ\text{C} \) show a weak and broad peak characteristic of amorphous structure (Fig. 1b and c).

In this article, we report high-performance, flexible OLEDs using an a-IZO anode grown by dc magnetron reactive sputtering at the temperature of \( <50^\circ\text{C} \) on a PC substrate. It was found that the a-IZO anode films deposited at \( <50^\circ\text{C} \) have similar conductivity, transparency, and surface smoothness as a commercial crystalline ITO (c-ITO) anode on glass prepared at high temperature (\( >300^\circ\text{C} \)). Furthermore, the OLEDs fabricated using the a-IZO anode on flexible substrates 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 (In2O3:ZnO = 90:10 wt %) and indium tin oxide target (In2O3:SnO2 = 90:10 wt %). The PC substrates (Glastic PC) have a glass transition temperature of \( \sim 150^\circ\text{C} \) and a coefficient of thermal expansion of 50–60 ppm/°C. The sputtering was carried out at a pressure of \( 4 \times 10^{-1} \text{ Pa} \) with a power of 1000 W. Argon mixed with oxygen was used as the reactive sputtering gas with the mixing ratio of O2/Ar = 0.04 and O2/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 \( <50^\circ\text{C} \) 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 \( 2\theta = 30.1^\circ \) (222), 35.20° (400), 50.44° (440), and 60.22° (622) in Fig. 1a. The XRD patterns of the IZO and ITO anode film deposited at \( <50^\circ\text{C} \) 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 \( <50^\circ\text{C} \) 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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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 is much lower than a-ITO/PC but higher than c-ITO/glass, which is similar to the recently reported results. 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.

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). However, the a-IZO film shows very small increase of resistance.

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.
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-IZO film. The robustness combined with the good electrical conductivity and high optical transparency of the a-IZO films deposited at <5°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 acetone and IPA. All organic layers were grown by thermal evaporation at the base pressure of <5 × 10⁻⁸ Torr in the following order: hole transport layer (HTL)/emission layer (EML)/hole blocking layer (HBL)/electron transport layer (ETL)/cathode. A 40 nm thick 4′,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) was used as the HTL, 30 nm thick a 1,3-bis(2-(1-naphthyl)-phenyl)hydrazino)benzene (BPP) was used as the ETL, 10 nm thick 2,2,3,3-tetrahydro-4,4-diphenyl-1,10-phenanthroline (BCP) as the HBL, and 40 nm thick tris(8-hydroxyquinoline) aluminum (Alq3) 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 OLEDs were measured simultaneously using a Keithley 2400 programmable source meter and 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 high 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.16,28 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 (∼5.2 eV) than that of c-ITO (∼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.

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