

## Enhanced performance of organic light-emitting devices by atmospheric plasma treatment of indium tin oxide surfaces

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Atmospheric plasma treatment of indium tin oxide (ITO) surfaces has been studied and demonstrated to be the most efficient method in improving the performance of vacuum-deposited double-layer organic light-emitting diode devices, among various plasma treatment methods including low-pressure Ar plasma and low-pressure O<sub>2</sub> plasma treatment. Although with a current–voltage characteristic close to low-pressure O<sub>2</sub> plasma treatment, the atmospheric plasma treatment exhibits a 40% increase of electroluminescence efficiency. X-ray photoelectron spectroscopy results show that the atmospheric plasma treatment increases the work function and reduces the carbon contamination of ITO surfaces. Our results suggest that atmospheric plasma treatment is a cheaper, more convenient, and more efficient method than low-pressure O<sub>2</sub> plasma treatment for improving device performance. © 2002 American Institute of Physics. [DOI: 10.1063/1.1428624]

Since Tang and Van Slyke reported the first vacuum-deposited, multilayer organic light-emitting diode (OLED) device in 1987,<sup>1</sup> OLED has received much attention over the last decade due to its great potential in low-cost, full-color flat-panel display. In the OLED devices with a typical structure of indium tin oxide (ITO)/triphenyl diamine (TPD)/tris(8-hydroxyquinolino) aluminum (ALQ)/aluminum (Al), both the barriers for electron injection and hole injection are important because the higher barrier will determine the current–voltage  $I$ – $V$  characteristic of the device and the lower one will determine the emission efficiency.<sup>2</sup> On the other hand, the aging of the device is not only dependent on the properties of organic layers, but also governed by the organic layer–electrode interface. At present, the poor device stability has been one of the major obstacles in realizing industrial applications. By using lithium fluoride (LiF)/Al composite cathode, electron injection barrier can be reduced to enhance the electron injection.<sup>3–5</sup> Besides, many approaches have been employed to pretreat the ITO surface in order to reduce the hole injection barrier and to remove the contaminants from the ITO surface. They include the wet treatment,<sup>6</sup> low-pressure plasma treatment,<sup>7–9</sup> UV ozone treatment,<sup>10</sup> and coating treatment with self-assembly monolayers.<sup>11</sup> Until now, the most effective method is low-pressure O<sub>2</sub> plasma treatment. However, the plasma treatment operated at low pressure has several drawbacks. Vacuum systems are usually expensive and have low throughput. Also, the size of the ITO substrate that can be treated is limited by the size of the vacuum chamber. Atmospheric plasma overcomes the aforementioned disadvantage of vacuum operation. Furthermore, higher plasma density and higher ozone density can be observed in the atmospheric plasma, e.g., in a dielectric barrier discharge.<sup>12</sup> Low energy ion bombardment of ITO surface is another advantage for atmospheric plasma due to high collision frequency in the gas and will prevent ITO surface from damages induced by

high energy ion bombardments. Yet no studies on the effects of ITO surface treatment by atmospheric plasma on the performance of OLEDs have been reported. In this work, we set up a dielectric barrier atmospheric plasma system in the laboratory and showed that the ITO surface treated by atmospheric plasma improved the device performance significantly.

Figure 1 describes the atmospheric plasma system employed in this study. It is a typical dielectric barrier type atmospheric plasma system by using a 13.56 MHz rf power supply to generate the plasma. The distance between the cathode and the anode is 4 mm. The ITO-coated glass substrate was supplied by Merck–Taiwan Corporation. The ITO

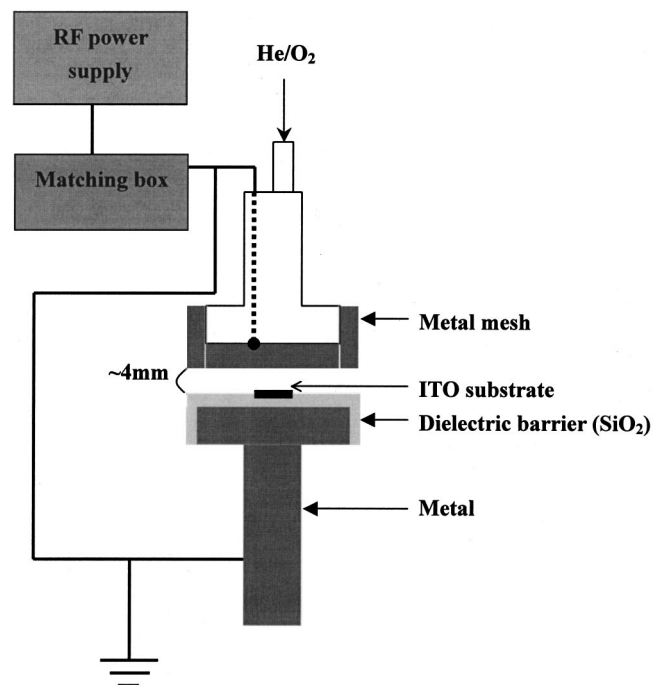


FIG. 1. Configuration of the dielectric barrier atmospheric plasma system employed in this study.

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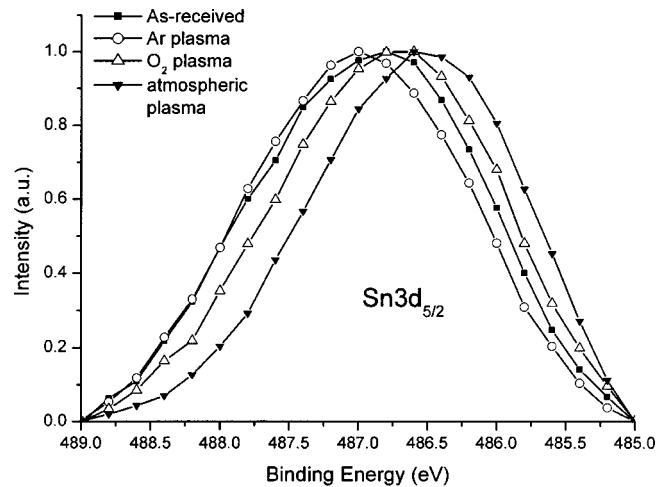
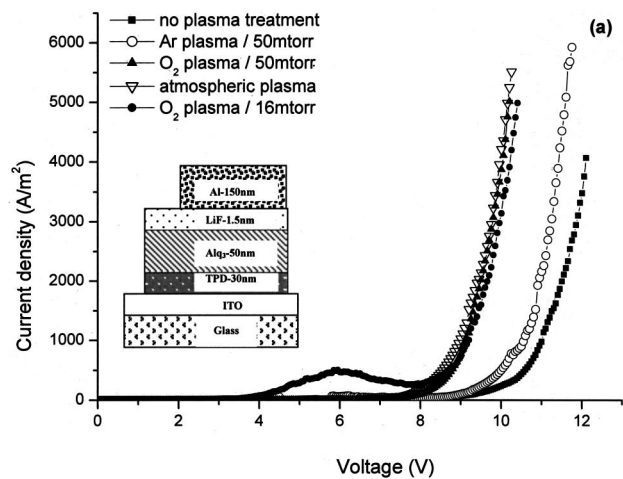
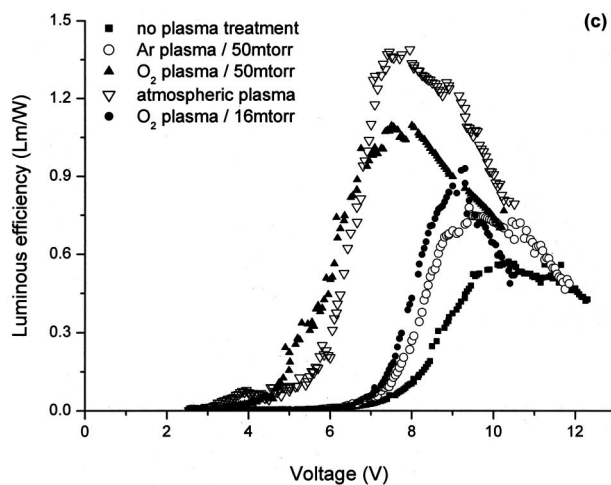
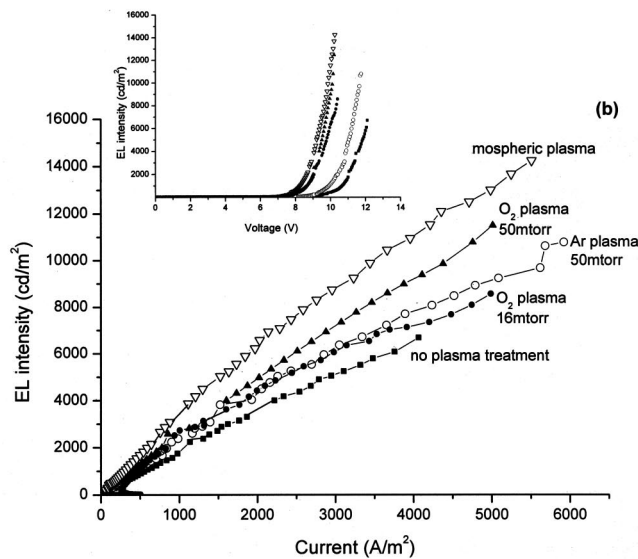
FIG. 3. Sn  $3d_{5/2}$  core level spectra for various ITO samples.

FIG. 2. Effects of ITO treatments on the performance of OLEDs: (a) current density versus applied voltage, (b) EL intensity versus current density, the inset showing EL intensity versus applied voltage, and (c) luminous efficiency versus applied voltage.

surface was first cleaned by the ethanol-impregnated paper with mechanical rubbing and then cleaned sequentially using the detergent, methanol and deionized (DI) water. Finally, the glass was rinsed in DI water and the ITO surface was dried by purging high purity nitrogen gas. The ITO-coated glass substrates were further treated by either atmospheric plasma for 5 min or low-pressure plasma using various gases

for 2 min before the deposition of organic layers. The device structure shown in the insert of Fig. 2(a) consists of glass/ITO/TPD (30 nm)/Alq<sub>3</sub> (50 nm)/LiF (1.5 nm)/Al (150 nm). TPD, Alq<sub>3</sub>, and LiF were deposited by thermal evaporation in a vacuum chamber with a base pressure of  $10^{-6}$  Torr. The deposition rates of the organic materials, LiF layer, and Al cathode were 1–2 Å/s, 0.1–0.2 Å/s, and 20 Å/s, respectively. The active area of the device was 8 mm<sup>2</sup>. The  $I$ – $V$  characteristics of the device was measured using a KEITHEY-2400 source meter and the luminance measured with a TOPCON BM-8 luminance meter. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Fison (VG) ESCA 21 system with Al  $K\alpha$  source with a photon energy of 1486.6 eV. Device performance was all measured in the air.

The  $I$ – $V$  behavior of electroluminescence (EL) devices fabricated with the plasma-treated ITO anodes are shown in Fig. 2(a). The turn-on voltage for the device was lowered significantly by atmospheric plasma treatment and low-pressure O<sub>2</sub> plasma treatment. For the device with low-pressure Ar plasma treatment or no plasma treatment, the turn-on voltages were between 10–12 V. The turn-on voltages decreased to 8 V for those with atmospheric plasma treatment or low-pressure O<sub>2</sub> plasma treatment. The reduction of turn-on voltages can be attributed to the removal of contaminants from ITO surface and the increase of ITO work function. A leakage current occurred at low voltages around 6 V for the ITO devices treated with low-pressure (16 mTorr) O<sub>2</sub> plasma, induced by the rough ITO surface as shown by the surface morphology measured by atomic force microscope (AFM). Figure 2(b) shows the EL intensity versus device current or voltage (see the insert). The highest EL emission intensity was observed for the atmospheric plasma treatment method at the same device current or voltage. For the same emission intensity, the much lower voltage and current suggested a much higher emission efficiency and less joule heating during device operation, resulting in the increase of operation durability of the device. Durability has been the most critical factor in all issues related with industrial applications of OLED. In Fig. 2(b), the EL intensity is shown to be linearly dependent on the device current. Since the slope of each line in Fig. 2(b) is proportional to its external quantum efficiency, the atmospheric plasma treatment

TABLE I. Atomic fractions of Sn<sup>+2</sup> and Sn<sup>+4</sup> on various ITO surfaces.

Atomic mole fractions	Treatment methods			
	As-received	Low-pressure Ar plasma	Low-pressure O <sub>2</sub> plasma	Atmospheric plasma
Sn <sup>+2</sup> (486.3 eV)	35%	30%	41%	52%
Sn <sup>+4</sup> (487.3 eV)	65%	70%	58%	48%

of ITO surface evidently enhances most the external quantum efficiency. The effects of the plasma treatments of ITO surface on OLED luminous efficiency (Lm/W) can be further clearly seen in Fig. 2(c). Note that the atmospheric plasma treatment resulted in the highest luminous efficiency ( $\sim 1.4$  Lm/W) and suggested that atmospheric plasma treatment can replace the traditional low-pressure O<sub>2</sub> plasma treatment for improving the performance of OLED devices.

Figure 3 shows the XPS spectra of Sn 3d<sub>5/2</sub> core levels recorded from various plasma treated ITO surfaces. It is clear that, in comparison with untreated ITO surface, there is a large spectral shift on ITO surface treated by atmospheric plasma, a smaller shift on the surface treated by low-pressure O<sub>2</sub> plasma and almost no shift on the surface treated by low pressure Ar plasma. The results of the deconvolution of XPS spectra in Fig. 3 are also shown in Table I. The reduction of Sn 3d<sub>5/2</sub> core electron binding energy after low pressure O<sub>2</sub> plasma or atmospheric plasma treatment indicates the decrease of Sn<sup>+4</sup> mole fraction and the increase of Sn<sup>+2</sup> mole fraction. The reduction of Sn<sup>+4</sup> donor concentration suggests a shift of n-type surface Fermi energy towards the middle of band gap and thus increases the work function of ITO surface.<sup>13</sup> The increase of ITO work function enhances the carrier injection and improves the device performance.<sup>14,15</sup> Therefore, atmospheric plasma treatment enhances the device performance most significantly. Furthermore, XPS measurements show that for the atmospheric plasma treatment the oxygen concentration in ITO surface is the highest and the carbon contamination level on ITO surface is the lowest. Low carbon contamination and high oxygen concentration also suggest a higher work function and better device performance.<sup>16,17</sup>

In conclusion, we have reported that atmospheric plasma treatment of ITO surface was a more efficient method than low-pressure O<sub>2</sub> plasma treatment by enhancing OLED emission efficiency from 1.0 to 1.4 Lm/W. XPS spectral shifts further indicated that atmospheric plasma treatment increased the work function and reduced the carbon contamination of ITO surface, thus enhancing the hole injection and improving the device performance. It is demonstrated that atmospheric plasma treatment of ITO surface is a cheaper, faster and more efficient method than low-pressure O<sub>2</sub> plasma treatment in enhancing OLED performance, and has a great potential to replace the traditional O<sub>2</sub> plasma method.

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