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Characteristics of Organic Light-Emitting Devices by the Surface Treatment of Indium Tin Oxide Surfaces Using Atmospheric Pressure Plasmas

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This study examined the effects of a He/O_2 and He/SF_6 atmospheric pressure plasma surface treatment of indium tin oxide (ITO) glass on the ITO surface and electrical characteristics of organic light emitting diodes (OLEDs). The OLEDs composed of ITO glass/2-TNATA/NPD/Alq_3/LiF/Al showed better electrical characteristics, such as lower turn-on voltage, higher power efficiency, etc., after the He/O_2 or He/SF_6 plasma treatment. The He/SF_6 treatment resulted in superior electrical characteristics compared with the He/O_2 treatment. The electrical improvement as a result of the He/SF_6 and He/O_2 plasma treatments is related to the decrease in the carbon and Sn^{4+} concentration on the ITO surface and fluorine doping of the ITO possibly indicating a change in the work function as a result of the treatments. [DOI: 10.1143/JJAP.44.L41]

KEYWORDS: ITO, surface treatment, atmospheric pressure plasma, OLED, He/O_2, He/SF_6

Organic light emitting diode (OLED) displays have been extensively studied due to their superior properties such as faster response time, lower operating voltage, higher quantum efficiency, etc. in addition to the simpler deposition processing and lower manufacturing cost compared with other flat panel displays such as liquid crystal displays and plasma display panels.[1–3] Currently, these devices are manufactured in a high vacuum chamber for substrate areas smaller than 370 mm × 470 mm using a multilayer evaporation technique for monomer organics, and deposition techniques for the large area substrates close to 920 mm × 730 mm are currently under development. In addition, OLED displays utilizing polymer organics, which use ink-jet printing instead of vacuum evaporation, are actively being studied.[4,5)]

On OLED devices, a transparent conductor is used for the higher optical transparency, and among the various transparent conductors, indium tin oxide (ITO) is the most widely used due to its high conductivity and transparency. In order to form OLED devices, the organic monomers are deposited on patterned ITO glass for the formation of a low resistive ohmic contact. The contact resistance between the ITO and organic materials of the OLED devices can be altered by the ITO surface preparation due to the organic materials on the ITO glass surface and the change in the ITO composition as a result of the ITO surface preparation method. ITO is a non-stoichiometric compound. Therefore, the chemical composition can be easily changed.[6] Consequently, in order to improve the contact properties between the ITO and the organic material of the OLED, the surface treatment of the patterned ITO before depositing the organic materials is very important.[6–13] As surface treatment methods, low pressure plasma techniques,[6–10,12] UV/O_3 techniques,[9–11] and wet treatments[12,13] have been used to remove the organic materials and improve the ITO surface properties. However, these techniques are expensive and difficult to scale to large areas using low pressure plasma and UV/O_3 techniques. In addition, there are environmental issues in the case of wet treatment.

Atmospheric pressure plasma such as a corona discharge,[14] dielectric barrier discharge (DBD),[15,16] atmospheric plasma jet,[17] etc. for the treatment of various surfaces applied to electric materials, electronic materials, biomaterials, structural materials, etc. have been actively studied in order to replace low pressure plasma techniques, wet processing, etc. This study examined the potential of using atmospheric pressure plasma for the surface treatment and cleaning of ITO glass for OLED devices. As an atmospheric pressure plasma cleaning technique, a modified DBD, which can be scaled to large areas and show a higher plasma density than conventional DBD, was used. By varying the gas mixture in the modified DBD, the effects of the gas mixture on the characteristics of the ITO surface and on the electrical properties of the OLED devices formed on the cleaned ITO glass were investigated.

Figure 1 shows a schematic diagram of the atmospheric pressure plasma equipment used in this study for the surface treatment of ITO glass. As shown in the figure, the modified DBD used in this study was composed of a pyramid shaped multi-pin electrode as the power electrode instead of a plate electrode, a plate electrode as the ground electrode, and dielectric materials on both electrodes. Using the multi-pin electrode instead of a blank plate electrode, a higher plasma density and gas breakdown at a lower AC voltage could be

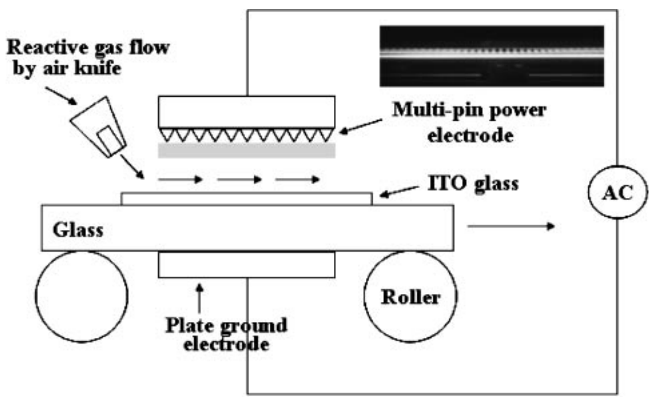

Fig. 1. Schematic diagram of the atmospheric pressure plasma equipment used for the surface treatment of ITO glass.

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obtained by forming a high electric field on the tip of the pins similar to the corona discharge with a higher stability and glow discharge shape instead of a filamentary discharge shape. The AC voltage in the range from 3 to 15 kV with a frequency of 20–30 kHz was connected to the multi-pin power electrode and the ground was connected to the plate ground electrode.

He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) were used as the ITO surface cleaning gas mixtures for the OLED devices. Before the plasma treatment, all the ITO glasses were cleaned with an organic solvent. These optimum gas compositions were selected after measuring the contact angle by a contact angle measuring tool and the carbon contents on the ITO surface by X-ray photoelectron spectroscopy (XPS, VG Microtech Inc., ESCA2000) after varying the O_2 flow rate from 0 to 3 slm and the SF_6 flow rate from 0 to 500 sccm with a He flow rate of 10 slm. The AC voltage used was 10 kV at 25 kHz and the processing time was 30 seconds. The composition of the ITO surface after cleaning with the He/O_2 and He/SF_6 plasma was investigated by XPS using Al Kα X-ray source of 1486.6 eV.

The OLED devices were fabricated on the cleaned ITO by the thermal evaporation of the OLED materials and electrode materials sequentially without breaking the vacuum. The OLED structure used in this study was ITO glass/2-TNATA(60 nm)/NPD(20 nm)/Alq_3(40 nm)/LiF(1 nm)/Al(100 nm). The deposition rates of the organic materials, LiF, and Al were 0.3–0.5 Å/s, 0.1 Å/s, and 0.5–5 Å/s, respectively. The fabricated device active area was 4 mm^2. The electrical characteristics of the fabricated OLED devices were measured using an electrometer (Keithley 2400) and the luminescence characteristics were determined by measuring the photocurrent induced by light emission from the OLEDs using a picoammeter (Keithley 485).

Figure 2 shows the characteristics of the OLEDs fabricated on the ITO glass cleaned by the atmospheric pressure plasma using the He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) gas mixtures such as (a) luminescence-voltage, (b) luminescence-current density, and (c) power efficiency-current density. As a reference, the characteristics of the OLED device fabricated without plasma cleaning were included. As shown in Fig. 2(a), the turn-on voltages of the devices (defined as the voltage required to deliver a luminescence of 1 cd/m^2) after the He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) treatment were 3.6 V and 3.2 V, respectively, while the turn-on voltage of the device without the plasma treatment was 4.2 V. Therefore, after the plasma treatment, the turn-on voltage was decreased and the He(10 slm)/O_2(3 slm) treatment showed a lower turn-on voltage than the He(10 slm)/SF_6(100 sccm) treatment. In addition, as shown in Fig. 2(b), the OLED treated by He(10 slm)/SF_6(100 sccm) showed the lowest current density at the same emission intensity while the OLED fabricated without the plasma treatment showed the highest current density. When the power efficiency was measured as a function of the current density, the highest power efficiencies were ~0.93 Lm/W, ~0.75 Lm/W, and ~0.58 Lm/W for the He(10 slm)/SF_6(100 sccm) treated sample, He(10 slm)/O_2(3 slm) treated sample, and the non-treated sample, respectively. Therefore, after the He(10 slm)/SF_6-(100 sccm) treatment, the device showed the best electrical performance.

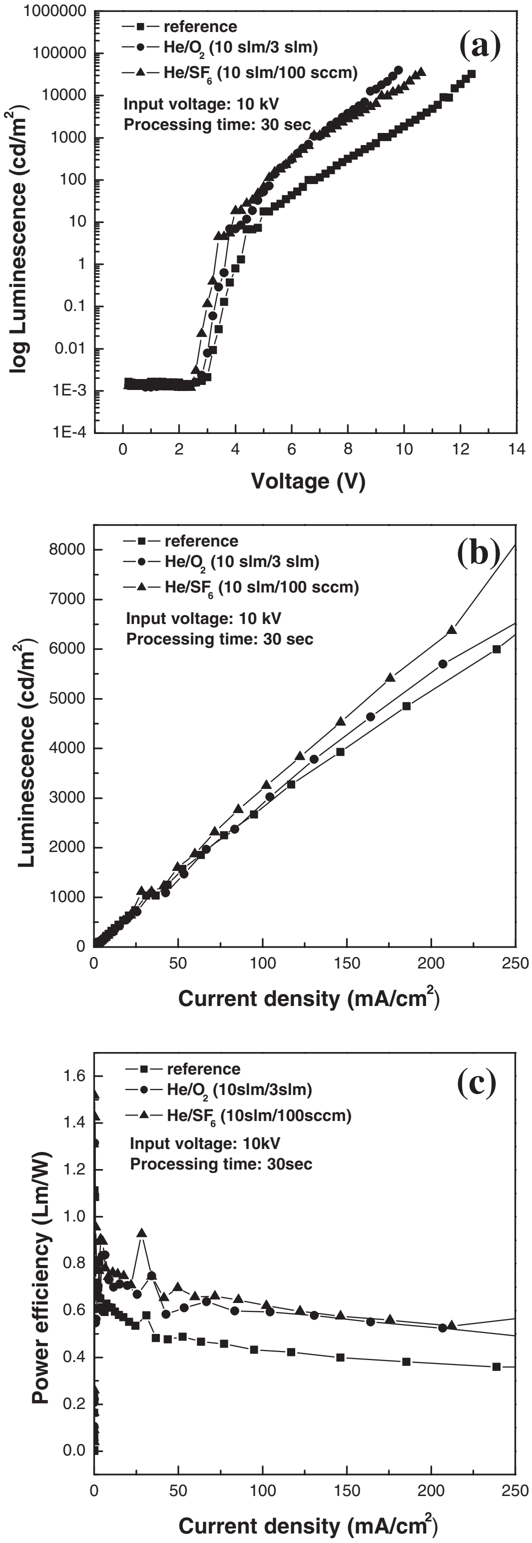

Fig. 2. Characteristics of the OLEDs fabricated on the ITO glass cleaned by the atmospheric pressure plasma using He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) gas mixtures. (a) luminescence-voltage, (b) luminescence-current density, and (c) power efficiency-current density. As a reference, the characteristics of the OLED device fabricated without plasma cleaning are included.

The improved electrical characteristics shown for the OLED after the He(10 slm)/SF_6(100 sccm) treatment appeared to be related to the removal of the remaining contaminants on the ITO surface and the change in the work

Table I. Composition of the ITO surfaces not treated (as is) and treated with He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) measured by XPS.

Treatment method	Atomic concentration (%)					
	C1s	$In3d_{5/2}$	$Sn3d_{5/2}$	O1s	F1s	Sn/In
As is	12.8	31.9	4.4	50.9		0.137
He/O_2 plasma (10 slm/3 slm)	9.2	32.2	4.2	54.4		0.130
He/SF_6 plasma (10 slm/100 sccm)	8.6	32.2	4.1	42.9	12.2	0.127

function of the ITO as a result of the plasma treatment. Table I shows the composition of the non-treated (as is) and He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) treated ITO surface measured by XPS. As shown in the table, carbon contamination on the surface decreased significantly as a result of the plasma treatment and the ITO surface after the He(10 slm)/SF_6(100 sccm) treatment showed the lowest carbon content on the surface. Therefore, the organic contaminants remaining after organic cleaning were removed further after the plasma cleaning, and the removal of the organic contaminants is believed to be partially responsible for the improved OLED performance.

In the case of the He(10 slm)/SF_6(100 sccm) cleaning, 12% of fluorine (F1s 685 eV) was detected on the ITO surface, which replaced oxygen on the surface when comparing the surface compositions of the ITO cleaned by the He(10 slm)/O_2(3 slm) and that by the He(10 slm)/SF_6(100 sccm). However, sulfur (S2p 164 eV) was not detected on the ITO surface as a result of the He(10 slm)/SF_6(100 sccm) treatment. The doping of fluorine on the ITO is known to improve the electrical properties of ITO similar to the doping of fluorine on SnO_2 by increasing the level of hole injection to the device.[8,19] In addition, in the XPS data, even though the Sn to In ratio was not significantly altered by the plasma treatment, the surface concentration of Sn^{4+} was deceased significantly by the plasma treatment. The $Sn3d_{5/2}$ peak can be deconvoluted into the: Sn^{2+}(486.3 eV) and Sn^{4+}(487.3 eV) oxidation states[7] and Fig. 3 shows the narrow scan XPS data of the deconvoluted Sn^{2+} and Sn^{4+} peaks of $Sn3d_{5/2}$ peak are shown in. As shown in the figure, the Sn^{4+} peak intensity was deceased by the plasma treatment and showed the lowest peak for the He(10 slm)/SF_6(100 sccm) treatment. It was reported that the substitution of an In^{3+} site by Sn^{4+} decreases the Sn^{4+} content and the decrease in Sn^{4+} increases the work function of ITO by changing the n-type Fermi level toward the middle of the band gap.[18] Therefore, the improvement in the OLED devices treated with the He(10 slm)/SF_6(100 sccm) is also related to the increase in the work function by the fluorination and the decrease in the Sn^{4+} level of the ITO in addition to the removal of carbon contaminants on the ITO surface.

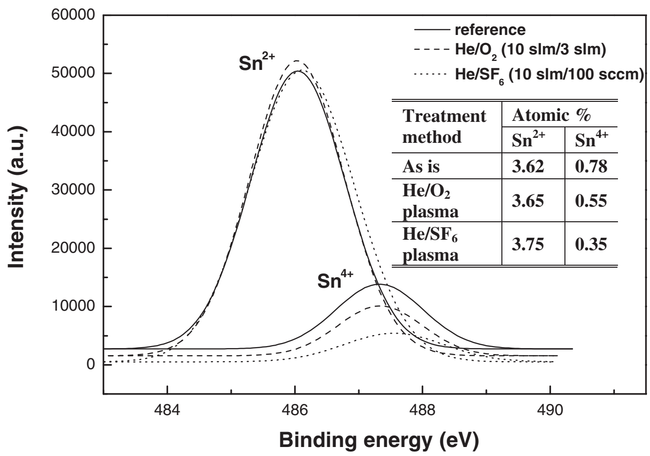

Fig. 3. Narrow scan XPS data of the deconvoluted Sn^{2+} and Sn^{4+} peaks from the $Sn3d_{5/2}$ peaks of the ITO surface treated with He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm). The XPS data of the ITO surface not treated by the plasma is also included.

In conclusion, the ITO glass surfaces were treated with He(10 slm)/O_2(3 slm) and He(10 slm)/SF_6(100 sccm) gas mixtures using an atmospheric pressure plasma equipment composed of a multi-pin type DBD and its effects on ITO surface properties and the characteristics of the OLED devices fabricated on the treated ITO were investigated. The OLED devices treated with the He(10 slm)/SF_6(100 sccm) plasma showed the best electrical properties such as the lowest turn-on voltage (He/SF_6 plasma treatment: 3.2 V, He/O_2 plasma treatment: 3.6 V, non-treatment: 4.2 V at the luminescence of 1 cd/m^2), highest luminescence at the same current density, and the highest power efficiency (He/SF_6 plasma treatment: 0.93 Lm/W, He/O_2 plasma treatment: 0.75 Lm/W, non-treatment: 0.58 Lm/W). The improved properties of the OLED devices after the ITO treatment using He(10 slm)/SF_6(100 sccm) appear to be related to the removal of the organic contaminants remaining on the ITO surface, the decrease in the Sn^{4+} level, and the fluorine doping on the ITO surface possibly indicating an increase in the work function of the ITO. Because atmospheric pressure plasma does not require a vacuum chamber, it can be installed easily in the loading chamber, and be scaled to substrates larger than 730 mm × 920 mm in size. It is believed that the use of He(10 slm)/SF_6(100 sccm) atmospheric pressure plasma can be successfully applied to a commercial OLED system requiring ITO cleaning. The effects of SF_6 on the ITO cleaning in low pressure plasma systems and a comparison with the data of the atmospheric pressure system are currently under investigation.

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