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Efficiency enhancement of the organic light-emitting diodes by oxygen plasma treatment of the ITO substrate

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Oxygen plasma has been treated on the surface of indium-tin-oxide (ITO) to improve the efficiency of the organic light-emitting diodes (OLEDs) device. The plasma treatment was expected to inject the holes effectively due to the control of an ITO work-function and the reduction of surface roughness. To optimize the treatment condition, a surface resistance and morphology of the ITO surface were investigated. The effect on the electrical properties of the OLEDs was evaluated as a function of oxygen plasma powers (0, 200, 250, 300, and 450 W). The electrical properties of the devices were measured in a device structure of ITO/TPD/Alq$_3$/BCP/LiF/Al. It was found the plasma treatment of the ITO surface affects on the efficiency of the device. The efficiency of the device was optimized at the plasma power of 250 W and decreased at higher power than 250 W. The maximum values of luminance, luminous power efficiency, and external quantum efficiency of the plasma treated devices increase by 1.4 times, 1.4 times, and 1.2 times, respectively, compared to those of the non-treated ones.

Key words: Plasma treatment, Surface resistance, Luminous power efficiency, External quantum efficiency.

Introduction

As the information technology advances, a trend is shifting to a flat-panel display. Organic light-emitting diode (OLED) is one of the candidates satisfying this trend [1]. Because the emissive materials in OLED are versatile, it can be applied to a display. And it has the advantages such as a low driving voltage, low power consumption, low cost, self light-emitting feature, full color capability, and etc [2]. In order to satisfy the stable operation, high luminance, and high efficiency of the OLED, a lot of studies are progressing in the areas of carrier injection [3], transport and light emission, electrode materials, interfacial contact between an electrode and organics [4], and highly efficient organic materials [5, 6]. Much efforts to improve the efficiency of the OLED has been made in many ways. One of the efforts is a pretreatment of the ITO surface, which is commonly used as a transparent anode in the device [7, 8]. Since the ITO has a advantages in electrical property, etching property and visible light transparency, it is widely used among the anode materials developed so far [9, 10]. However, there are some problems to be considered in ITO. In particular, it was reported that when the bias voltage or the optical power is applied to OLEDs or organic photovoltaic cells, an interface between the ITO surface and the organic layer affects on the efficiency of the OLEDs [11, 12].

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Depending on the physical and chemical treatments of the ITO surface, the interfacial properties are significantly changed [13]. There are several ways of surface treatments such as a thermal, chemical, electrochemical, and plasma processing method [6, 13]. In general, it was reported that the oxygen (O_2) plasma treatment shows an improvement in the reformation of interface between the ITO surface and the organic layer. Thus, the oxygen plasma treatment of ITO surface gives the improvements in hole injection in the anode and smooth morphology of the ITO surface, which is expected to improve the efficiency and lifetime of the OLEDs [14, 15].

In this study, an efficiency enhancement of the OLEDs was investigated by treating the ITO surface with the oxygen plasma. Optimum plasma power for the ITO surface treatment was obtained by measuring the resistance and morphology of the ITO layer surface [16]. After comparing the plasma treated ITO surface with the non-treated one obtained from the above measurements, it was applied to the devices.

Experimental

N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) was used as a hole-transport material and tris(8-hydroxy-quinolinato)aluminium (Alq$_3$) was used as an emissive material. In addition, bathocuproine (BCP) and lithium fluoride (LiF) were used as an electron-transport and electron-injection material, respectively. The ITO substrate was cut to a size of 100×100 mm^2. After taping the section of 5 mm in width for the anode, the remaining part was etched by exposing it to the vapor of a solution mixed with a volume ratio of 3 : 1 of hydrochloric acid and nitric acid for 30 minutes. Afterwards, the patterned ITO substrate was cut into a size of 20×20 mm^2, and then cleaned. The cleaning process is as follows; at first, the substrate was ultrasonically cleaned in acetone for about 25 minutes at a temperature of 50 °C. And then, the substrate was ultrasonically cleaned again in a solution that was made by mixing hydrogen peroxide, ammonia, and secondary de-ionized water with a volume ratio of 1 : 1 : 5 for one hour at a temperature of about 80 °C. After that, the substrate was ultrasonically cleaned in acetone for 20 minutes at 50 °C. And finally, the substrate was ultrasonically cleaned in isopropyl alcohol and primary de-ionized water, respectively, for about 20 minutes each. And then it was dried using nitrogen gas [17].

The patterned ITO surface was treated with oxygen plasma using the equipment (Femto Sciences Co.). After plasma treated at a power of 0, 150, 200, 250, 300, and 450 W, it was baked for 30 minutes on a hot plate. In addition, after plasma treated at a power of 250 W from 20 to 60 seconds in a step of 10 seconds interval, it was baked for 30 minutes on a hot plate. To see how the plasma treated ITO affects on the device performance, the OLEDs were manufactured by the thermal vacuum deposition. Fig. 1 shows a device structure of ITO/TPD/Alq_3/BCP/LiF/Al. Depositions of TPD, Alq_3, and BCP were carried out at a deposition rate of 1 Å/s to make a thickness of 40 nm, 60nm, and 5 nm, respectively, under a pressure of approximately 5×10^{-6} torr. And the LiF was deposited to a thickness of 0.5 nm at a rate of 0.1 Å/s under a pressure of about 5×10^{-6} torr. Al cathode was deposited using a tungsten boat under a pressure of approximately 5×10^{-6} torr at a rate of 0.5 ~ 1.0 Å/s to a thickness of first 10 nm, and at a rate of about 10 Å/s later to a thickness of 100 nm. For the electrical measurements of the device, a four-point probe method meter, atomic force microscope (AFM), Keithley 2000 multimeter, 6517 electrometer, and DC power supply (Vupower Co.) were used. Labview software was used in controlling the equipments for a measurement of the voltage, current, luminance, luminous power efficiency, and external quantum efficiency of the samples.

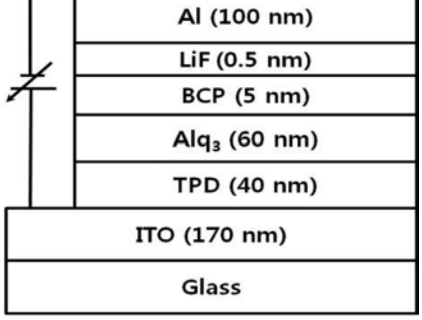

Fig. 1. Device structure used in this experimental work.

Results and discussion

In order to find an optimum oxygen plasma power for the ITO surface treatment, the surface resistance of the ITO surface was measured using a four point-probe method [16]. Fig. 2 shows the average surface resistance of the ITO substrates as a function of the oxygen plasma treatment power. The surface resistance was measured at ten different positions on the ITO surface to obtain the average values. Several plasma powers were employed and a treated time was 20 seconds. The obtained average surface resistances of the ITO surface were 25.74, 25.44, 23.22, 21.99, 23.11, and 31.42 Ω/sq for the plasma power of 0, 150, 200, 250, 300, and 450 W, respectively. As shown in Fig. 2, the surface resistance decreases up to 250 W and then increases again, indicating that, when the oxygen plasma power is 250 W, the surface resistance is superior to the others. It is thought that the oxygen plasma treatment contributes to an enhancement in reforming the ITO surface and a reduction in the surface resistance up to the power of 250 W. However, at the higher plasma power than 250 W, the surface resistance increases probably due to a severe damage on the ITO surface by oxygen molecules.

Fig. 3 represents a graph relating the surface resistance of the ITO surface made at the plasma power of 250 W as a function of the treatment time. The treatment time was varied from 20 to 60 seconds in order to find the optimal condition. It was found that the surface resistances of the ITO surface are 21.99, 20.81, 17.64, 21.81, and 25.42 Ω/sq for the plasma treatment time of 20, 30, 40, 50, and 60 seconds, respectively. It is seen that the surface resistance of the ITO surface decreases up to 40 seconds and then increases rapidly above 40 seconds. This behavior could be considered as the same origin as that in Fig. 2.

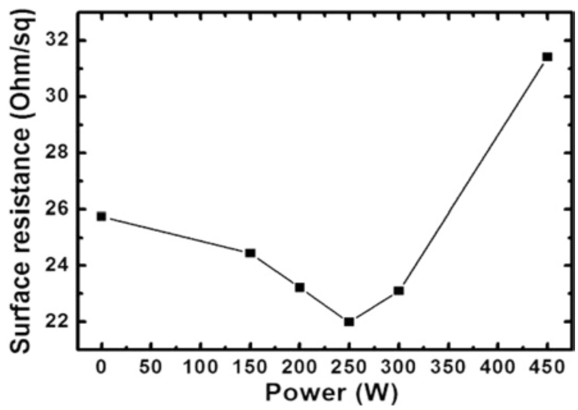

Fig. 2. Surface resistance of the ITO substrate depending on the plasma treatment power.

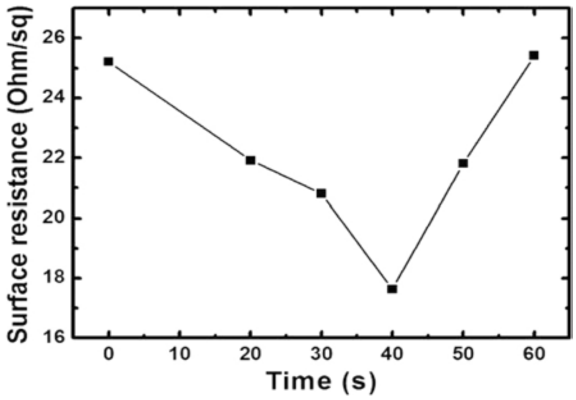

Fig. 3. Surface resistance of the ITO substrate depending on the plasma treatment time.

As the plasma treatment time increases to 40 second, it may contribute to a reformation of the surface and a reduction in the surface resistance. However, when the treatment time is above 40 seconds, oxygen molecules may affect on the ITO surface, and the surface resistance increases. From Figs. 2 and 3, the average surface resistance of 17.64 Ω/sq was obtained at the oxygen plasma treatment power of 250 W for a treatment time of 40 seconds.

Fig. 4 shows the atomic-force microscope (AFM) images of the ITO surface taken to relate the measured resistance and morphology of the surface. Fig. 4(a) ~ (f) reveal that an average surface roughness of 3.17, 2.26, 2.17, 1.39, 1.68, and 1.62 nm for the ITO surfaces treated with plasma power at 0, 150, 200, 250, 300, and 450 W, respectively. Plasma treated time was 40 seconds in all cases. The obtained average surface roughness of the plasma treated ITO surface is listed in Table 1. The surface roughness of the plasma treated ITO at 250 W is approximately 44% lower compared to that of the non-treated one. But, the average surface roughness of

Table 1. Average surface roughness of the ITO surface depending on the plasma treatment power.

Plasma treatment power (W)	Average roughness (nm)
0	3.17
150	2.26
200	2.17
250	1.39
300	1.68
450	1.62

the ITO surface increases when the plasma power is above 250 W. This is thought to be attributed to oxygen molecules penetrating to the ITO surface, and it causes an increase of the surface roughness.

Electrical properties of the OLEDs were investigated using the oxygen plasma treated ITO substrate. Fig. 5(a) shows a current density and luminance of the device as a function of the applied voltage for several plasma powers. Voltage-dependent current density and luminance were measured simultaneously. It was found that the device with plasma treated ITO shows a reduction in turn-on voltage and an increase in luminance compared to those of the non-treated ITO. An increase in luminance is thought to be related to a reduction in the surface roughness of the ITO substrate by treating with the plasma. An improvement in the interfacial property might lower the hole injection energy barrier, and then it may help a recombination of electrons and holes even at low applied voltage. While the maximum luminance out of the non-plasma treated device is 6,374 cd/m^2 at 10 V, the maximum luminance of the plasma treated at 250 W is 8,626 cd/m^2 at 9 V.

The maximum luminance and corresponding voltage of the device for several plasma powers is summarized

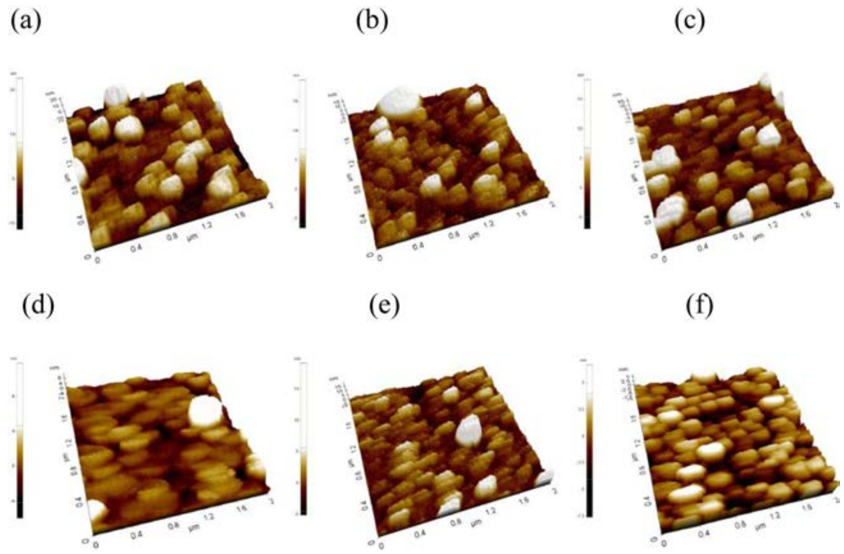

Fig. 4. AFM images of ITO substrate depending on the plasma treatment power of (a) 0 W, (b) 150 W, (c) 200 W, (d) 250 W, (e) 300 W, and (f) 450 W.

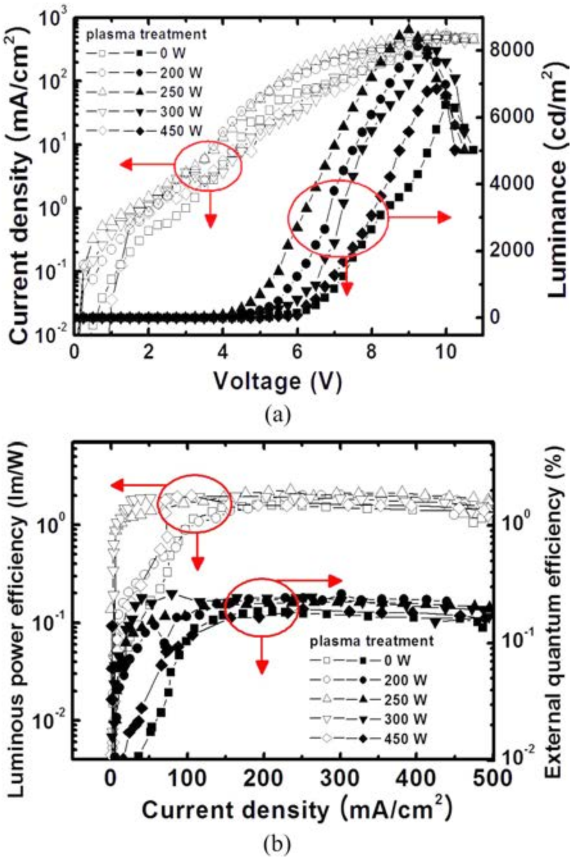

Fig. 5. Electrical properties of the OLEDs depending on the plasma treatment power. (a) J-V-L characteristics and (b) J-ς_p-ς_{ext} characteristics.

in Table 2. It shows that the maximum luminance out of the device with the surface treated ITO at 250 W is higher than that of the one with non-treated ITO by 1.4 times, and the applied voltage for the maximum luminance is smaller by 1 V. It was found that the device with the ITO surface treated at 250 W shows a higher luminance and a lower turn-on voltage compared to the others.

Fig. 5(b) shows an external quantum efficiency and luminous power efficiency of the OLEDs depending on the plasma power. It is seen that the external quantum efficiency and the luminous power efficiency increase rapidly in the current density region of 0 ~ 100 mA/cm^2 and then increase slowly above that region. In general, the efficiency in the device with oxygen plasma treated ITO is higher than the one without plasma treated. Table 3 lists the maximum luminous power efficiency and external quantum efficiency for several plasma powers. It was found that the maximum luminous power efficiency and external quantum efficiency of the device with plasma treated ITO at 250 W are higher than those of the one without plasma treated by 1.4 and 1.2 times, respectively. From the analysis of the electrical properties of the device, the device with plasma treated ITO at 250 W showed excellent electrical characteristics.

Table 2. Maximum luminance of the device and corresponding applied voltage depending on the plasma treatment power.

Plasma treatment power (W)	Maximum luminance (cd/m^2)	Applied voltage (V)
0	6,374	10
200	8,129	9.25
250	8,626	9
300	7,995	9.75
450	6,856	9.75

Table 3. Maximum luminous power efficiency and external quantum efficiency of the device depending on the plasma treatment power.

Plasma treatment power (W)	Luminous power efficiency (lm/W)	External quantum efficiency (%)
0	1.61	0.185
200	2.01	0.215
250	2.29	0.223
300	1.96	0.209
450	1.92	0.194

Conclusions

In order to improve the efficiency and electrical properties of the device, it was aimed at lowering of energy barrier height at the interface between the ITO surface and hole-transport layer for an efficient hole injection. From a study of electrical properties of the ITO surface treated by oxygen plasma, it was found that the surface resistance of the ITO is superior to the others when the ITO is treated under a plasma power of 250 W for 40 seconds, and the surface resistance under these conditions is about 17.64 Ω/sq. And it was also found the average surface roughness is superior to the others when the ITO is treated under a plasma power of 250 W for 40 seconds, and the surface roughness under these conditions is about 1.39 nm. Therefore, it could be concluded that the efficiency of the device is superior to the others when the ITO surface is plasma treated at 250 W. The obtained maximum values of luminance, luminous power efficiency, and external quantum efficiency were 8,626 cd/m^2, 2.29 lm/W, and 0.223%, respectively. As a result, the device with a use of plasma treated ITO gives an improvement in the maximum values of luminance, luminous power efficiency, and external quantum efficiency by a factor of 1.4, 1.4, and 1.2 compared to those of the device with non-treated ITO. Thus, we have found that the oxygen plasma treatment of the ITO surface affects on the electrical properties of the OLEDs. It is thought that the improvement in the device efficiency is related to a lowering of the surface resistance and smoothness of the surface by performing an oxygen plasma treatment of the ITO surface.

Acknowledgements

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