

Study on the O₂ Plasma Treatment of Indium Tin Oxide for Organic Light Emitting Diodes Using Inductively Coupled Plasma

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In this study, the effect of O₂ inductively coupled plasma (ICP) conditions for the indium tin oxide (ITO) surface treatment on the organic light emitting diode (OLED) device performances were investigated. By the O₂ plasma treatment of ITO glass, better OLED device performances such as a lower turn-on voltage, a higher luminescence, and a higher power efficiency could be obtained and the use of lower oxygen pressure and higher ICP power improved the device properties further. DC-biasing of the ITO glass substrate degraded the device properties. The use of lower oxygen pressure and higher ICP power increased the densities of O₂⁺ and O* in the plasma, and the plasma-treated ITO surface showed a lower carbon, a higher O/(Sn + In), and a higher Sn⁴⁺/In for the condition of lower oxygen pressure and higher ICP power. The improved OLED device properties with the ITO treated at the higher ICP power and the lower pressure appear to be from the increased hole injection to the OLED materials by decreasing the resistance of ITO and by increasing the work function of the ITO.

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1. Introduction

Organic light emitting diodes (OLEDs) have been extensively studied for flat panel display devices due to their superior properties such as faster response time, lower operating voltage, higher quantum efficiency, etc. in addition to simpler deposition processing and lower manufacturing cost compared with other devices for flat panel displays such as liquid crystal displays and plasma displays.^{1,2)} Currently, these devices are manufactured in a high vacuum chamber for the substrate areas smaller than 370 × 470 mm² using a multilayer evaporation technique for monomer organics, and the deposition techniques for the large area substrates close to 920 × 730 mm² are currently under development. In addition, OLED devices utilizing polymer organics, which are deposited by ink-jet printing instead of vacuum evaporation, are actively being studied.^{3,4)}

For the OLEDs 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, organic monomers are deposited on the 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 an ITO surface treatment. ITO is a non-stoichiometric compound, therefore, the chemical composition can be easily changed by the surface treatment.⁵⁾ Consequently, to improve the contact properties between the ITO and the organic material of the OLEDs, the surface treatment of the patterned ITO before depositing the organic materials is very important.^{6–13)} As the ITO surface treatment methods, low pressure plasma techniques,^{5–11,14)} UV/O₃ techniques,^{10–12)} atmospheric pressure plasma techniques,^{5,13)} and wet treatment techniques^{14,15)} have been used to remove organic contaminants and to improve the ITO surface properties. Among the above techniques, O₂ low pressure plasma treatment is most widely used to fabricate OLED devices, however, the optimization of the

O₂ plasma condition and the mechanism for the low resistive ohmic contact by the O₂ plasma treatment are not well investigated.

Therefore, in this study, using O₂ inductively coupled plasmas (ICP), the optimized process condition for the ITO surface treatment such as pressure, source power, and dc bias voltage and the relation of the low resistive ohmic contact to the plasma characteristics and the ITO surface composition were investigated.

2. Experimental

Figure 1 shows the schematic diagram of the ICP used for the ITO surface treatment in this experiment. To generate ICP, 13.56 MHz rf power was fed to the five-turn spiral-type Au-coated copper tubing on the 10 mm thick quartz window located on the top of the process chamber and, to induce dc-bias voltage, a separate 13.56 MHz rf power was fed to the water-cooled 6 inch diameter substrate holder. The distance between the top quartz plate and the bottom substrate was about 75 mm. On the sidewall of the process chamber, a quartz view port was installed for the optical emission spectroscopy (OES).

As the sample, 150 nm thick ITO coated glass substrates having the sheet resistance of 12–15 Ω/square were used. Before the O₂ plasma treatment, the ITO glass substrates were cleaned by wet solutions in the sequence of acetone, ethanol, and de-ionized water in a ultrasonic cleaner. For the plasma treatment, 10 and 100 mTorr of the operation pressures were used by controlling the throttle valve while flowing 50 sccm of O₂. The rf power to the ICP source was varied from 100 to 500 W. For some of the cases, –150 V of dc-bias voltage was applied to the substrate to study the effect of ion bombardment. Also, to study the effect of ion bombardment further, one of the ITO glass substrates was treated with –550 V of dc-bias voltage at 100 mTorr without applying ICP source power. The plasma treatment time was kept for 30 seconds. On the plasma treated ITO glass substrate, a series of materials was deposited by thermal evaporation to form a green-light emitting OLED composed of ITO glass/2-TNATA (60 nm)/NPD (20 nm)/Alq₃ (40 nm)/LiF (1 nm)/Al (100 nm) and to investigate the emission

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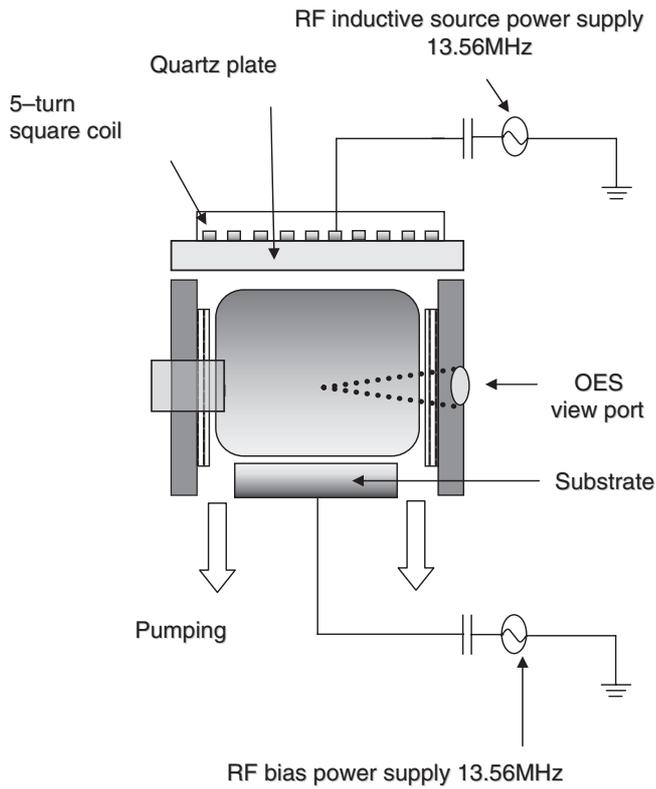


Fig. 1. Schematic diagram of the ICP equipment use for the surface treatment of ITO glass.

characteristics. The active area of the fabricated OLED device was 4 mm^2 .

The electrical characteristics of the fabricated OLED devices were measured by the Keithley 2400 electrometer and the luminescence characteristics of the OLEDs were measured with a photodiode (Oriel 71608) and Keithley 485 picoammeter. The characteristics of O_2 plasma were measured by OES (SC Technology, PCM 402) installed on the sidewall of the chamber and the species such as O_2 ions (O_2^+) and O radical (O^*) were measured. The surface characteristics of the O_2 plasma treated ITO glass substrates were characterized by X-ray photoelectron spectroscopy (XPS; VG Microtech, ESCA2000) using an Al $K\alpha$ source with the photon energy of 1486.6 eV.

3. Results and Discussion

Figure 2 shows the characteristics of (a) luminescence–voltage (L – V), (b) luminescence–current density (J – V), and (c) power efficiency–current voltage (P – J) of the OLED devices fabricated on the O_2 plasma treated ITO glass with the operational pressure of 10 and 100 mTorr and with the ICP source power of 100 and 500 W. As a reference, the characteristics of the OLED device fabricated on the ITO glass without plasma treatment was included. As shown in Fig. 2(a), the turn-on voltage (defined as the voltage needed to deliver a luminescence of 1 cd/m^2) of the OLED device treated with 10 mTorr/500 W was the lowest (3.0 V), those treated with 10 mTorr/100 W and 100 mTorr/500 W was 3.2 V, and that treated with 100 mTorr/100 W was 3.6 V. The turn-on voltage of the OLED device with untreated ITO glass was the highest (4.8 V). Therefore, by the O_2 plasma treatment, a lower turn-on voltage could be obtained and the

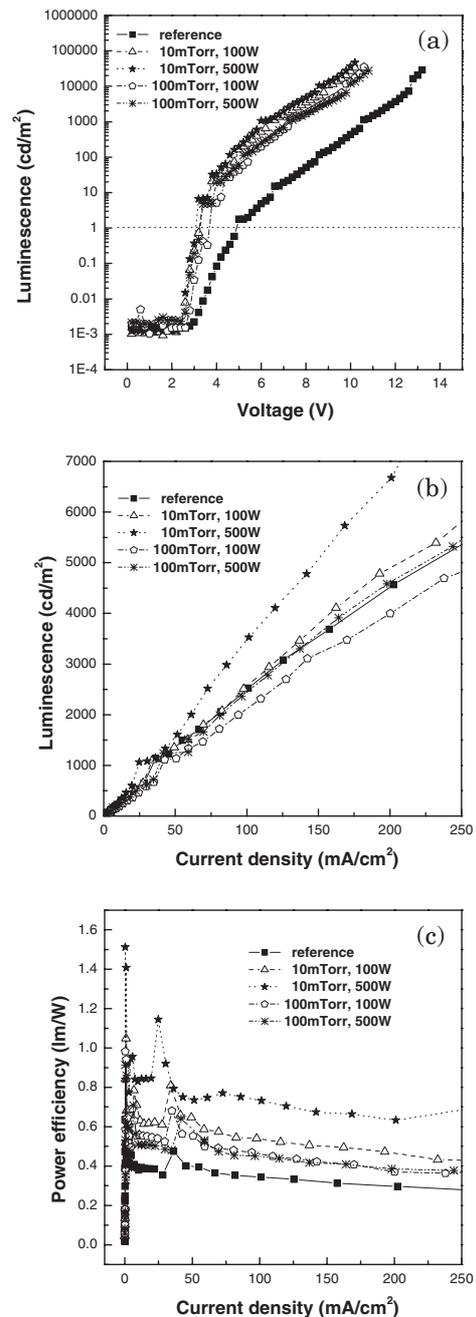


Fig. 2. Characteristics of (a) luminescence–voltage (L – V), (b) luminescence–current density (J – V), and (c) power efficiency–current voltage (P – J) of the OLED devices fabricated on the O_2 plasma treated ITO glass with the operational pressure of 10 and 100 mTorr and with the ICP source power of 100 and 500 W. As a reference, the characteristics of the OLED fabricated on the ITO glass without plasma treatment was included.

use of the O_2 plasma at the lower pressure/higher ICP source power showed the lower turn-on voltage. Also, the device treated with 10 mTorr/500 W showed the highest luminescence of $46,000\text{ cd/m}^2$ at 10 V.

The L – J curves shown in Fig. 2(b) also showed the similar trend as the L – V curves in Fig. 2(a). The OLED devices fabricated on the O_2 plasma treated ITO glass generally showed the higher luminescence at the same current density possibly due to the higher emission efficiency and the lower joule heating.⁵⁾ Also, the devices treated with 10 mTorr/500 W showed the highest lumines-

cence at the same current density. The devices treated with other plasma conditions showed the similar L - J characteristics to the device fabricated without the plasma treatment. When the P - J of the devices were calculated, as shown in Fig. 2(c), similar to the case in Fig. 2(a), the power efficiency was higher in the sequence of untreated (max: ~ 0.5 lm/W) $<$ 100 mTorr/100 W (max: ~ 0.7 lm/W) \approx 100 mTorr/500 W $<$ 10 mTorr/100 W (max: ~ 0.81 lm/W) $<$ 10 mTorr/500 W (max: ~ 1.2 lm/W). Therefore, the OLED device fabricated on the ITO glass treated with the O_2 plasma at the lower pressure and the higher power showed the better OLED device properties.

The characteristics of the OLED devices fabricated on the ITO glass treated in the O_2 plasma with/without biasing the substrate at -150 V to study the effect of ion bombardment were carried out. (not shown) The O_2 plasma was generated at 10 mTorr of operational pressure and with 300 and 500 W of ICP power. Also, the characteristics of the device treated with -550 V of dc-bias voltage at 100 mTorr without applying ICP source power was included. By biasing the ITO glass substrate at -150 V, the turn-on voltage was increased from 3.0 to 3.4 V for 300 W and from 3.0 to 3.6 V for 500 W. When -550 V of dc-bias voltage was applied at 100 mTorr without applying the ICP source power, the turn-on voltage was about 3.9 V. Therefore, even though the turn-on voltages of the devices treated in the plasmas with biasing were lower than the voltage of the device with untreated ITO (4.8 V), the application of dc-bias voltage, that is, the ion bombardment of the ITO glass substrate increased the turn-on voltage. In the case of the overall L - V characteristics, the devices treated with dc-biasing showed similar or worse L - V characteristics compared to the device with untreated ITO glass. Especially, the device treated at -550 V showed much lower luminescence compared to the untreated device at the same voltage. In the case of L - J curve, the devices treated in the O_2 plasmas with bias voltage of -150 or -550 V did not show significant differences in the luminescence at a constant current density compared to the device with untreated ITO. The P - J characteristic shows the effect of biasing during the ITO plasma treatment more clearly. The power efficiency of the devices treated in the plasmas with the biasing was similar to that of untreated device (~ 0.5 lm/W). Therefore, the biasing the ITO glass at -150 or at -550 V during the plasma treatment did not improve the device characteristics.

The variation of the device characteristics with the ITO treated in the plasma with the different pressures and ICP powers appears to be partially related to the oxygen radicals (O^*) and oxygen ions (O_2^+) in the plasma. Figure 3 shows the O_2^+ (563.2 nm) and O^* (616 nm) measured for 10 and 100 mTorr as a function of ICP power using OES. The O_2^+ and O^* measured for 10 mTorr with biasing the substrate at -150 V were included in the figure. As shown in the figure, the OES intensities of O_2^+ and O^* were higher for 10 mTorr compared to those for 100 mTorr and the biasing the substrate did not change the OES intensities. Also, the increase of the ICP source power increased the OES intensities. The increase of O_2^+ and O^* at the lower pressure appears to be related to the higher power efficiency of ICP source at the lower pressure. No significant change of O_2^+ and O^* by biasing the substrate is from the insignificant effect of the substrate

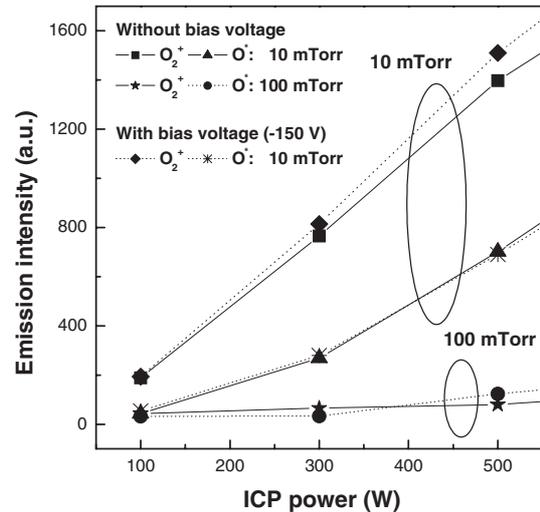


Fig. 3. Emission intensities of oxygen ions (O_2^+) and oxygen radicals (O^*) measured by OES for the O_2 plasma operation conditions shown in manuscript.

biasing on the dissociation and ionization of the gas in the plasma. When the results in Fig. 3 are compared with those in Fig. 2, the better device characteristics appear to be related to the higher OES intensities of O_2^+ and O^* in the plasma indicating larger amount of the reactive species of oxygen in the plasma. It is well known that O_2^+ and O^* can easily react with In or Sn atoms in the ITO thin film to form metal oxides, resulted in the reduction of oxygen vacancies in the films. Therefore, the larger number of O_2^+ and O^* in the plasma is believed to improve the device properties by modifying the ITO surface composition.

The atomic composition and the component ratios of the ITO surface after the O_2 plasma treatments were investigated using XPS and the results are shown in Table I. As a reference, the atomic composition and the component ratios of the as-received (wet cleaned) ITO surface were included. As shown in the table, the use of O_2 plasma decreased the carbon percentage on the ITO surface and the ITO surface treated at the lower pressure and higher ICP power showed the lower carbon percentage. The ITO surface treated with the plasma at 10 mTorr/500 W without the dc-biasing showed the lowest carbon percentage of 3.9%. The lower carbon percentage remaining on the ITO surface treated at the lower pressure and higher ICP power appears to be related to the higher intensities of O_2^+ and O^* observed by OES. Therefore, the removal of organic materials by the O_2 plasma on the ITO surface is related to the improvement of the device performances. In addition, as shown in the table, the ITO treated at the lower operational pressure and higher ICP power showed a higher ratio of O/(In + Sn) and a lower ratio of Sn^{4+} /In resulting in the decrease of oxygen vacancy and the decrease of electron donors, respectively.¹³⁾ It is known that the decrease of oxygen vacancy and electron donors on the ITO surface will decrease the carrier concentration and will increase the work function of the ITO.⁶⁻⁸⁾ Therefore, the higher ratio of O/(In + Sn) and the lower ratio of Sn^{4+} /In obtained at the higher ICP power and lower operational pressure also appear to improve the device performances by increasing hole injection to the OLED materials from the ITO through the higher work function.

Table I. Atomic composition and the component ratios of the ITO surface after various O₂ ICP treatments investigated by XPS. As a reference, the atomic composition and the component ratios of the as-received (wet cleaned) ITO surface were included.

Treatment method			Atomic concentration (%)		Ratio		
			C 1s	O 1s	In/Sn	O/(In + Sn)	Sn ⁴⁺ /In
Reference			26.1	44.5	7.65	1.51	0.025
Pressure (mTorr)	Source power (W)	Bias voltage (V)					
10	100	0	6.7	60.3	7.46	1.83	0.014
	300	0	4.9	64.2	7.83	2.08	0.013
	500	0	3.9	68.5	7.9	2.48	0.012
	300	-150	10.0	49.3	11.33	1.21	0.018
	500	-150	7.4	52.2	10.88	1.29	0.018
100	100	0	7.8	52.3	8.07	1.31	0.014
	300	0	8.0	53.2	7.62	1.37	0.014
	500	0	5.8	57.7	7.69	1.58	0.013
	0	-550	9.1	50.4	10.57	1.24	0.016

As shown in the table, the carbon percentage on the ITO surfaces treated by the plasmas with biasing the substrate was higher than that treated without biasing the substrate at the same operational pressure and the same ICP power. The higher carbon percentage on the ITO surface treated by the plasma with biasing might be related to the increased recontamination of the ion bombarded ITO surface during the air exposure. Also, a lower ratio of O/(In + Sn) and the higher ratio of In/Sn of the ITO surface with biasing are believed to be related to the preferential sputtering of oxygen and indium by ion bombardment even though the intensities of O₂⁺ and O* in the plasma are similar for the cases with/without biasing as shown in Fig. 3. The lower ratio of Sn⁴⁺/In for the conditions with biasing might be related to the ITO surface damage. The lower ratio of O/(In + Sn), the lower ratio of Sn⁴⁺/In, and the more surface contamination for the conditions with biasing can increase the work function and the ITO contact resistance, therefore, the poor performances appear to be obtained with the OLED device fabricated on the ITO treated in the plasma with biasing the substrate.

4. Conclusions

In this study, the effect of O₂ ICP conditions such as ICP power, pressure, and biasing the substrate for the ITO surface treatment on the OLED device performances fabricated on the plasma treated ITO were investigated. The OLED devices fabricated on the plasma treated ITO glass substrate showed a lower turn-on voltage, a higher luminescence, and a higher power efficiency compared to the devices fabricated on the untreated ITO. Also, the use of lower oxygen pressure and higher ICP power improved the device properties. However, the plasma treatment of the ITO glass with biasing at -150 V (or at -550 V) decreased the performances of the fabricated OLED devices. The use of lower oxygen pressure and higher ICP power increased the densities of O₂⁺ and O* in the plasma, therefore, the decrease of carbon contamination, the increased ratio of O/(Sn + In), and the increased ratio of Sn⁴⁺/In of the ITO surface could be obtained. The improved OLED devices with the ITO treated at the higher ICP power and the lower operational pressure appears to be from the increased hole

injection to the OLED materials by decreasing the resistance of ITO and by increasing the work function of the ITO. However, the dc-biasing of the ITO glass during the plasma treatment decreased the ratio of O/(In + Sn) and increased the ratio of In/Sn possibly due to the preferential sputtering. Also, the biasing the ITO glass at -150 V (or -550 V) increased the ratio of Sn⁴⁺/In possibly due to the damage of the ITO surface.

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- 1) C. W. Tang and S. A. VanSlyke: Appl. Phys. Lett. **51** (1987) 913.
- 2) G. Parthasarathy, P. E. Burrows, V. Khalfin, V. G. Kozlov and S. R. Forrest: Appl. Phys. Lett. **72** (1998) 2138.
- 3) S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott: Appl. Phys. Lett. **70** (1997) 2067.
- 4) J. C. Carter, I. Grizzi, S. K. Heeks, D. J. Lacey, S. G. Latham, P. G. May, O. R. Delospanos, K. Pichler, C. R. Towns and H. F. Wittmann: Appl. Phys. Lett. **71** (1997) 34.
- 5) I. M. Chan, W. C. Cheng and F. C. Hong: Appl. Phys. Lett. **80** (2002) 13.
- 6) H. Y. Yu, X. D. Feng, D. Grozea, Z. H. Lu, R. N. S. Sodhi, A. M. Hor and H. Aziz: Appl. Phys. Lett. **78** (2001) 2595.
- 7) J. S. Kim, F. Cacialli, A. Cola, G. Gigli and R. Cingolani: Appl. Phys. Lett. **75** (1999) 19.
- 8) D. J. Milliron, I. G. Hill, C. Shen, A. Kahn and J. Schwartz: J. Appl. Phys. **87** (2000) 572.
- 9) B. Choi, H. Yoon and H. H. Lee: Appl. Phys. Lett. **76** (2000) 412.
- 10) C. C. Wu, C. I. Wu, J. C. Sturm and A. Kahn: Appl. Phys. Lett. **70** (1997) 1348.
- 11) X. M. Ding, L. M. Hung, L. F. Cheng, Z. B. Deng, X. Y. Hou, C. S. Lee and S. T. Lee: Appl. Phys. Lett. **76** (2000) 2704.
- 12) B. L. Low, F. R. Zhu, K. R. Zhang and S. J. Chua: Thin Solid Films **417** (2002) 116.
- 13) C. H. Jeong, J. H. Lee, Y. H. Lee, N. G. Cho, J. T. Lim, C. H. Moon and G. Y. Yeom: Jpn. J. Appl. Phys. **44** (2005) L41.
- 14) J. S. Kim, R. H. Friend and F. Cacialli: Appl. Phys. Lett. **74** (1999) 3084.
- 15) F. Nuesch, L. J. Rothberg, E. W. Forsythe, Q. T. Le and Y. Gao: Appl. Phys. Lett. **74** (1999) 880.