

Effects of inductively coupled plasma treatment using O₂, CF₄, and CH₄ on the characteristics of organic light emitting diodes

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Abstract

In this study, the effects of indium tin oxide (ITO) surface treatment by various inductively coupled plasmas using O₂, CF₄, and CH₄ on the device characteristics of the organic light emitting diodes (OLEDs) consisted of ITO glass/2-TNATA/ α -NPD/Alq₃/LiF/Al were investigated. Among the various plasma treatments, the treatment by the CF₄ plasma showed the best OLED device characteristics while the treatment by the CH₄ plasma showed the worst OLED characteristics. The best OLED device characteristics obtained with the CF₄ plasma treatment was believed to be related to the decrease of hole injection barrier by the formation of a thin CF_x buffer layer between the ITO and OLED material in the OLED device. Also, it was believed to be related to the decrease of hole injection property by the increase of work function and the decrease of resistance of ITO with the increase of the (O+F)/(In+Sn) ratio and the decrease of the Sn⁴⁺/In ratio on the ITO surface after the CF₄ plasma treatment. The OLED device obtained after the ITO surface treatment by the CF₄ plasma decreased the turn-on voltage from 4.8 to 3.0 V, increased the highest power efficiency from ~0.58 to 1.35 lm/W, and increased the highest luminescence from 29,000 to 50,000 cd/m².

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1. Introduction

The organic light-emitting diodes (OLEDs) have attracted much attention in recent year [1–3], and are currently considered one of the most promising candidates for full-color flat panel display devices. On the conventional 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 small molecules are deposited on the patterned ITO glass for a low resistive ohmic contact and, to construct efficient devices, it is important to improve the carrier injection ability from the ITO electrode [4]. The contact resistance between the ITO and organic materials of the OLEDs devices can be altered by the surface treatments such as the surface cleaning of ITO surface and the deposition of a thin buffer layer between the ITO and the

organic molecules. The ITO surface cleaning by O₂ plasmas has been used to change the contact resistance by altering the ITO surface composition during the ITO surface treatment. In the case of buffer layers, various buffer layers including CuPc [5], SiO_x [6], Teflon [7], PEDOT:PSS [8], and fluorocarbon coatings (CF_x) [9] have been used to improve the hole injection property at the ITO/organic materials interface. In the case of CF_x deposition, it is known that the conductivity of CF_x coating is sensitive to deposition conditions and has a low reproducibility [9].

Even though various ITO surface treatment techniques were carried out to improve the contact resistance, the mechanisms having a low resistance by the surface treatments are not clear and it is still required to develop a simpler and more reliable process for a low ITO contact resistance. Therefore, in this study, to investigate a simple method of ITO surface treatment for a low contact resistance and to study its mechanism, the ITO surface was treated by inductively coupled plasma (ICP) using various gases such as O₂, CF₄, and CH₄ to alter the surface of ITO and their effects on the OLED device characteristics were investigated.

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2. Experiments

Fig. 1 shows the schematic diagram of the ICP used for the ITO surface treatment in this experiment. To generate the ICP, 13.56 MHz rf power was fed to the 5-turn spiral-type Au-coated copper tubing on the 10 mm thick quartz window located on the top of the process chamber. The distance between the top quartz window plate and the bottom substrate was about 75 mm.

As the sample, 150 nm thick ITO coated glass substrates having the sheet resistance of 12–15 Ω /square were used. Before the plasma treatment, the ITO glass substrates were cleaned by wet solutions in the sequence of acetone, ethanol, and de-ionized water using an ultrasonic cleaner. For the plasma treatment, 500 W of rf power was applied to the ICP source while flowing 50 sccm of gas at 10 mTorr of operation pressure. The process gases investigated were O_2 , CF_4 , and CH_4 . The plasma treatment time was kept for 30 s. On the plasma treated ITO glass substrates, a series of materials was deposited by thermal evaporation to form a green-light emitting OLED composed of ITO glass/2-TNATA (60 nm)/ α -NPD (20 nm)/Alq₃ (40 nm)/LiF (1 nm)/Al (100 nm) and to investigate the emission characteristics. The active area of the fabricated OLED device was 4 mm².

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 surface characteristics of the plasma treated ITO glass substrates were characterized by X-ray photoelectron spectroscopy (XPS,

VG Microtech Inc., ESCA2000) using an Al K α source with the photon energy of 1486.6 eV.

3. Results and discussion

Fig. 2(a) shows the current density and the luminescence measured as a function of voltage for the OLEDs fabricated after the plasma surface treatment of ITO surface using various gases such as O_2 , CF_4 , and CH_4 at 50 sccm of gas flow rate, 10 mTorr of operating pressure, 500 W of ICP source power for 30 s. As shown in Fig. 2(a), except for the CH_4 plasma, the plasma surface treatment by O_2 and CF_4 decreased the turn-on voltage (defined as the voltage needed to deliver a luminescence of 1 cd/m²) and increased the current density and luminescence at a given voltage. The highest luminescence of 50,000 cd/m² was obtained at 10.6 V by the CF_4 plasma treatment, 46,000 cd/m² at 10.2 V by the O_2 plasma treatment, and 29,000 cd/m² at 13.2 V for the non-treated ITO. In the case of the OLED device with the ITO treated with the CH_4 plasma barely emitted light (max. luminescence \approx 300 cd/m²).

Details of the turn-on voltages for the OLED devices in Fig. 2(a) are shown in Fig. 2(b). As shown in the figure, the lowest turn-on voltage was about 3.0 V for the treatment by both the O_2 plasma and the CF_4 plasma and was lower than that of non-plasma treated OLED device (4.8 V). However, the OLED device treated by the CH_4 plasma showed the highest turn-on voltage of 17.8 V. At the same luminescence, as shown in Fig. 2(c), the lowest current density was obtained by the

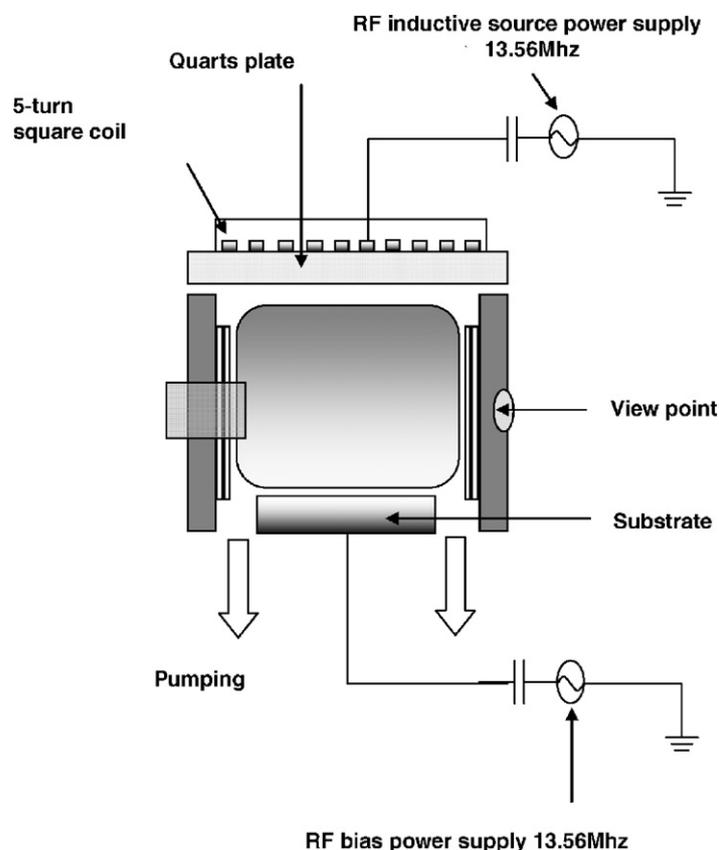


Fig. 1. Schematic diagram of the ICP equipment for the surface treatment of ITO glass.

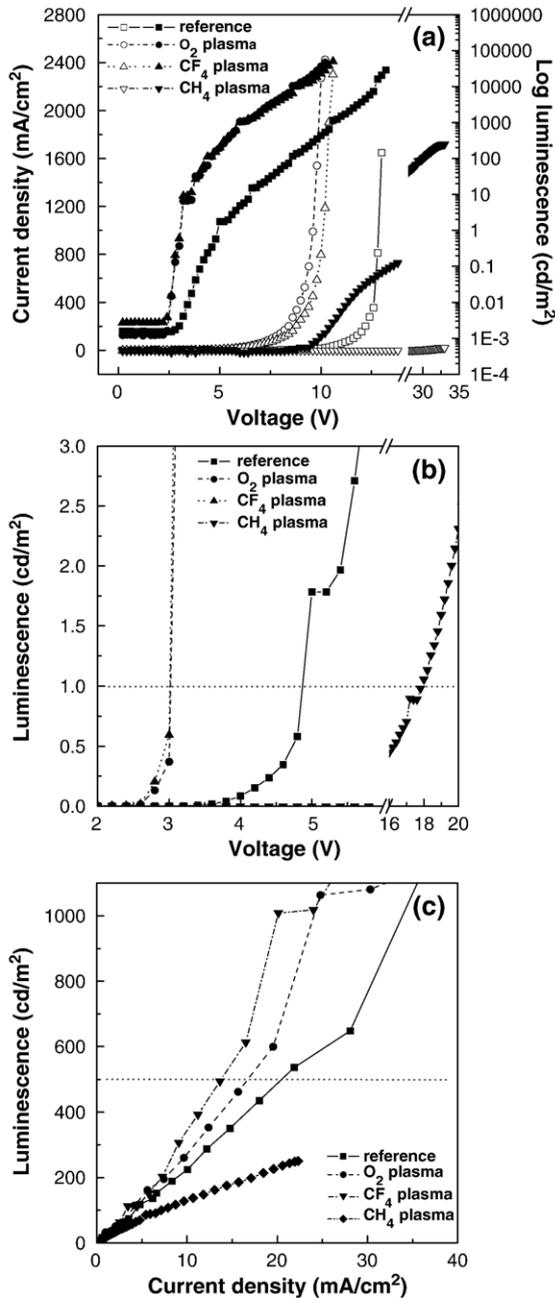


Fig. 2. Characteristics of OLEDs fabricated on the ITO glass treated by the ICPs using various gases such as O₂, CF₄, and CH₄. (a) current density–luminescence–voltage, (b) luminescence–voltage, and (c) luminescence–current density. As a reference, the characteristics of the OLED device fabricated without the plasma treatment were included.

OLED device treated by the CF₄ plasma and was followed by in the sequence of the O₂ plasma treatment, non-treatment, and the CH₄ plasma treatment. The lower turn-on voltages and the lower current densities at the same luminescence obtained with the OLED devices treated by O₂ plasma and CF₄ plasma compared with those obtained without ITO treatment (non-treated) appear to be related to the removal of contaminants on the ITO surface and the increase of work function by the ITO surface modification. Also, the decrease of current density at the same luminescence of the device by the treatment using the O₂

plasma and the CF₄ plasma decreases the joule heating of the device during the device operation, therefore, the operation durability of the device is believed to be increased by the treatment [10].

Fig. 3 shows the external quantum efficiency (a) and the power efficiency (b) measured as a function of current density of the devices shown in Fig. 2(a). As shown in the figure, the OLED treated by the CF₄ plasma showed the highest quantum and power efficiencies of ~0.9% and ~1.35 lm/W, respectively, at 20 mA/cm² of current density. For the O₂ plasma treated OLED, the highest quantum and power efficiencies of 0.75% and ~1.15 lm/W, respectively, were obtained at 24.8 mA/cm² while the highest efficiencies of 0.55% and ~0.48 lm/W, respectively, were obtained at 1000 cd/m² of luminescence. For the CH₄ plasma treated OLED, due to the low light emission, it was difficult to measure the efficiencies. Therefore, except for the CH₄ plasma treated OLED, the plasma treatment improved the OLED device characteristics and the CF₄ plasma treatment showed the best OLED characteristics.

The change of OLED device characteristics with the plasma treatment of ITO surface was investigated by studying the ITO surface composition before and after the plasma treatment using

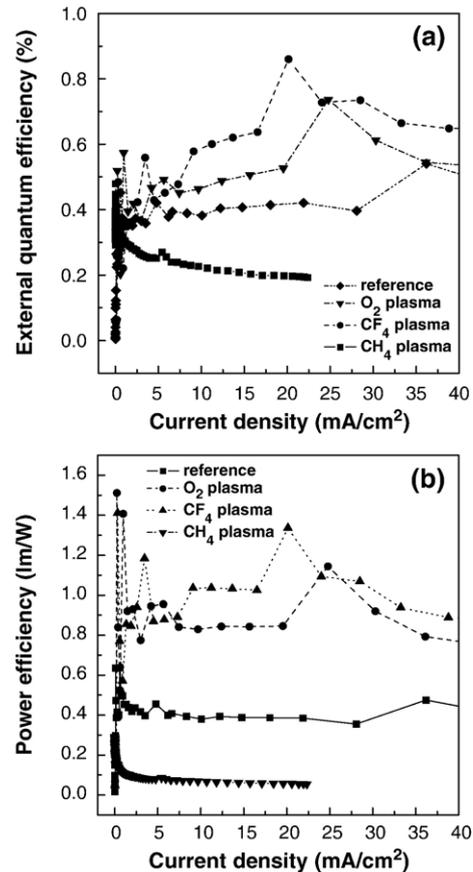


Fig. 3. Characteristics of OLEDs fabricated on the ITO glass treated by the ICPs using various gases such as O₂, CF₄, and CH₄. (a) external quantum efficiency–current density and (b) power efficiency–current density. As a reference, the characteristics of the OLED device fabricated without the plasma treatment were included.

XPS. The results are shown in Table 1. As shown in the table, carbon percentage on the ITO surface was decreased significantly by the plasma treatment using O₂ and CF₄ except for the treatment by CH₄. (In the case of CH₄, most of surface was composed of carbon possibly due to the formation of a carbon layer on the surface) In addition, the plasma treatment by O₂ and CF₄ increased the O₂ percentage on the ITO surface without significantly changing the percentages of In and Sn. Also, the ratios of (O+F)/(In+Sn) were increased and Sn⁴⁺/In were decreased by the ITO surface treatment using O₂ and CF₄. In the case of ITO surface treated by the CF₄ plasma, 12.7% of F was observed on the ITO surface. The decrease of carbon percentage and the increase of oxygen percentage of the ITO surface after the treatment by O₂ and CF₄ appear to be related to the decrease of contamination on the ITO surface. In addition, the increase of (O+F)/(In+Sn) and the decrease of Sn⁴⁺/In obtained by the plasma treatment of O₂ and CF₄ are known to increase the ITO work function by decreasing carrier concentration through the decrease of oxygen vacancies and electron donors [11–14]. Therefore, the improvement of OLED device characteristics obtained by the plasma treatment of O₂ and CF₄ are believed to be related to the improvement of hole injection from ITO to the organic materials of the OLED by the higher work function obtained with higher (O+F)/(In+Sn) and lower Sn⁴⁺/In after the treatment by O₂ and CF₄. Also, the worst OLED characteristics obtained after CH₄ plasma treatment appears to be related to the carbon contamination of the ITO surface.

Fig. 4 shows the XPS narrow scan data of C 1s (285 eV) on the ITO surfaces before and after the treatment by the plasma using O₂, CF₄, and CH₄. All the C 1s peaks showed the peak at 285 eV corresponding to C–C bonding. In the case of CF₄ plasma treated ITO, in addition to the peak related to the C–C bonding, the peak related to C–F bonding could be observed at 289 eV possibly indicating the formation of a thin CF_x layer on the ITO surface. Tong et al. [9] showed that, while the hole injection barrier from ITO to α -NPD is 0.68 eV for the ITO/ α -NPD interface, the hole injection barriers from ITO to α -NPD are 0.6 and 0.46 eV for the interfaces composed of ITO/CF_x/ α -NPD and ITO/UV-treated CF_x/ α -NPD, respectively. Therefore, the better OLED device characteristics obtained by the CF₄ plasma treatment compared to those by the O₂ plasma treatment appear to be related to the lower hole injection barrier by the formation of a thin buffer CF_x layer between the ITO and the organic material of the OLED during the CF₄ plasma treatment. In addition, the increase of hole injection property from the ITO to the organic material of the OLED obtained by the CF₄ plasma treatment may be partially related to the fluorine doping to ITO

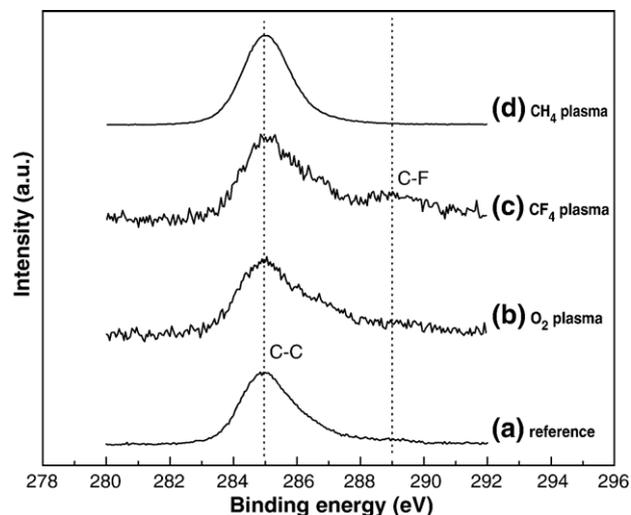


Fig. 4. Narrow scan XPS data of the C 1s peaks of the ITO surfaces treated by O₂, CF₄, and CH₄ plasmas. The XPS data of the non-treated ITO surface was also included.

as reported by Anderson et al. [15] for fluorine doping to tin oxide.

4. Conclusion

In this study, the surface of the ITO, used as the anode of OLED device, was plasma treated by ICP using O₂, CF₄, and CH₄ before the deposition of organic materials for OLED and the effects of the ITO plasma treatment on the characteristics of OLEDs fabricated after the treatment were investigated. The treatment of ITO by the CF₄ plasma and O₂ plasma showed the better OLED device characteristics compared to the non-treated OLED device while the treatment by the CH₄ plasma showed the worse OLED characteristics than the non-treated device. The better OLED device characteristics obtained by the plasma treatment of O₂ and CF₄ were believed to be related to the improvement of hole injection property by the increase of work function with the increase of the (O+F)/(In+Sn) ratio and the decrease of the Sn⁴⁺/In ratio. The device characteristics of the OLED treated by the CF₄ plasma were better than those treated by the O₂ plasma possibly due to the decrease of hole injection barrier by the formation of a thin CF_x buffer layer between the ITO and the organic material of the OLED device and possibly due to the increase of hole injection property of ITO by the fluorine doping. The OLED device obtained after the ITO surface treatment by the CF₄ plasma decreased the turn-on

Table 1
Composition of the ITO surfaces measured by XPS before and after the treatment by the plasma using O₂, CF₄, and CH₄

Treatment method	Atomic concentration (%)							
	C 1s	In 3d _{5/2}	Sn 3d _{5/2} (Sn ²⁺ +Sn ⁴⁺)	O 1s	F 1s	In/Sn	(O+F)/(In+Sn)	Sn ⁴⁺ /In
Reference	26.1	26	3.4	44.5	0	7.65	1.51	0.025
O ₂ plasma	3.9	24.5	3.1	68.5	0	7.9	2.48	0.012
CF ₄ plasma	7.1	23.3	3	53.9	12.7	7.77	2.53	0.012
CH ₄ plasma	96	0	0	4	0			

voltage from 4.8 V to 3.0 V, increased the highest power efficiency from ~ 0.58 lm/W at 36.2 mA/cm² to 1.35 lm/W at 20 mA/cm², and increased the highest luminescence from $29,000$ cd/m² at 13.2 V to $50,000$ cd/m² at 10.6 V. The worse OLED device characteristics after the CH₄ plasma treatment was related to the formation of a carbon layer on the ITO surface.

Acknowledgments

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References

- [1] C.W. Tang, S.A. VanSlyke, *Appl. Phys. Lett.* 50 (1987) 913.
- [2] G. Parthasarathy, P.E. Burrows, V. Khalfin, G.G. Kozlov, S.R. Forrest, *Appl. Phys. Lett.* 72 (1998) 17.
- [3] J.T. Lim, N.G. Cho, C.H. Jeong, J.H. Lee, J.H. Lim, G.Y. Yeom, *J. Korean Phys. Soc.* 47 (2005) 142.
- [4] L.S. Huang, C.W. Tang, *Appl. Phys. Lett.* 74 (1999) 3209.
- [5] J. Kido, Y. Iizumi, *Appl. Phys. Lett.* 73 (1998) 2721.
- [6] Z.B. Deng, X.M. Ding, S.T. Lee, W.A. Gambling, *Appl. Phys. Lett.* 74 (1999) 2227.
- [7] Y. Qiu, Y. Gao, L. Wang, D. Zhang, *Synth. Met.* 130 (2002) 235.
- [8] W.H. Kim, A.J. Makinen, N. Nikolov, R. Shashidhar, H. Kim, Z.H. Kafafi, *Appl. Phys. Lett.* 80 (2002) 3844.
- [9] S.W. Tong, C.S. Lee, Y. Lifshitz, D.Q. Gao, S.T. Lee, *Appl. Phys. Lett.* 84 (2004) 4032.
- [10] I.M. Chan, W.C. Cheng, F.C. Hong, *Appl. Phys. Lett.* 80 (2002) 13.
- [11] H.Y. Yu, X.D. Feng, D. Grozea, Z.H. Lu, R.N.S. Sodhi, A.-M. Hor, H. Aziz, *Appl. Phys. Lett.* 78 (2001) 2595.
- [12] J.S. Kim, F. Cacialli, A. Cola, G. Gigli, R. Cingolani, *Appl. Phys. Lett.* 75 (1999) 19.
- [13] D.J. Milliron, I.G. Hill, C. Shen, A. Kahn, J. Schwartz, *J. Appl. Phys.* 87 (2000) 572.
- [14] C.H. Jeong, J.H. Lee, Y.H. Lee, N.G. Cho, J.T. Lim, C.H. Moon, G.Y. Yeom, *Jpn. J. Appl. Phys.* 44 (2005) L41.
- [15] A. Anderson, N. Johansson, P. Broms, N. Yu, D. Lupo, R. Salaneck, *Adv. Mater.* 10 (1998) 859.