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[a]Display and Nanosystem Laboratory, College of Engineering, Korea University, Seoul 136-713, Republic of Korea

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Abstract

In this paper, we focused on the effects of the plasma treatment of the anode electrode of organic light emitting diodes (OLED) on the growth of hole-injection layer (HIL). The CF_4 plasma

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ABSTRACT

In this paper, we focused on the effects of the plasma treatment of the anode electrode of organic light emitting diodes (OLED) on the growth of hole-injection layer (HIL). The CF_4 plasma (CF_4-P) treatment, which is known for efficient method to enhance the performance of OLED, was not effective on the OLED with the HIL material copper phthalocyanine (CuPc). The CF_4-P treated OLED showed remarkably reduced electroluminescence (EL) characteristics while the O_2 plasma treated OLED showed improved EL efficiency. The dependence of the CuPc growth on the polarity of substrate induced the morphological difference of the HIL, and finally resulted in the different device characteristics.

1. Introduction

Nowadays, surface modification of indium tin oxide (ITO) transparent anode electrode is an essential process for the fabrication of organic light-emitting diodes (OLED). One of the most widely used technologies is plasma treatment. The doped single-layer poly(N-vinylcarbazole) OLED having ITO treated with different plasma including argon (Ar-P) and oxygen (O_2-P) showed the improved device stability and current efficiency followed by driving voltage drops but not with the hydrogen plasma (H_2-P) [1]. And the OLED having the ITO/triphenyldiamine showed the improved current and power efficiency when it was treated with Ar-P, carbon tetrafluoride (CF_4-P), O_2-P, and CF_4-P/O_2-P [2]. And also, the OLED with the hole-injection layer (HIL) 4,4′,4″-Tris(N-(2-naphthyl)-N-phenyl-amino) triphenylamine showed the improved current and power efficiency when the ITO was treated by the O_2-P, and CF_4-P, but not with the methane plasma [3]. Another recently introduced air plasma treatment by Lee et al. [4], also improved the current injection property of OLED having the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) as the HIL. Most recently, Huang et al. reported that the OLED having the plasma treated ITO/N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) showed the current efficiency in the order of un-treated≈Ar-P≈H_2-P>O_2-P>CF_4-P, and the power efficiency in the order of CF_4-P»O_2-P>Ar-P>un-treated>H_2-P [5]. It has been suggested that the enhanced performance is mainly due to a reduced hole-injection barrier at the ITO/organic interface. But, according to the above mentioned reports, the enhancements by the plasma treatment depend on not only the kind of plasma, but also the kind of organic material which is deposited on the ITO. In this paper, we systematically investigated the effect of the plasma treatment of HIL on OLED performance, specifically the growth of organic molecular.

2. Experimental

In this work, the two OLED devices with CF_4-P and O_2-P treated ITO and one control OLED device without treatment were examined.

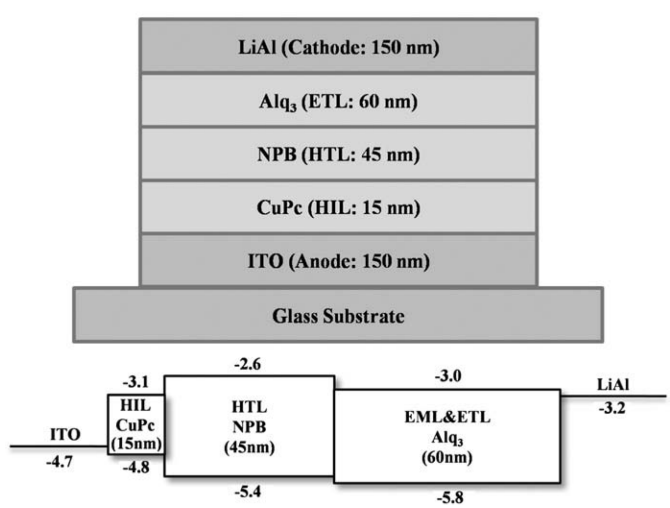

Fig. 1. The structure and energy band diagram of the OLEDs.

* Corresponding author. Tel.: +82 2 3290 3237; fax: +82 2 3290 3791.
E-mail address: bkju@korea.ac.kr (B.K. Ju).
URL: http://diana.korea.ac.kr (B.K. Ju).

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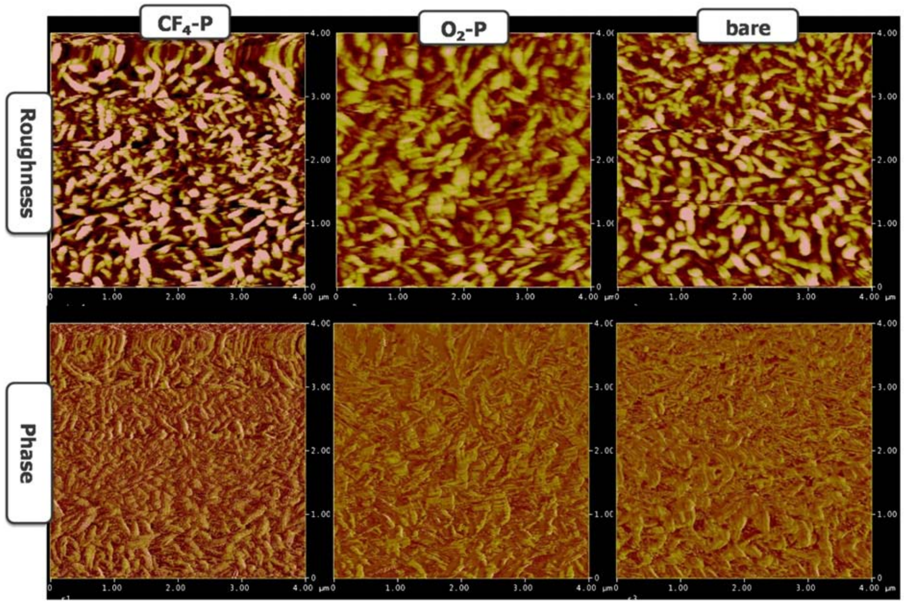

Fig. 2. The SPM images of the CuPc thin films on different plasma treated ITO substrates.

The device structure and energy band diagram are shown in Fig. 1 which is similar to that of the Reference [6]. The indium tin oxide (ITO) was used as a transparent anode; copper phthalocyanine (CuPc), as a hole injection layer; NPB, as a hole transport layer; tris–(8-hydroxyquinoline) aluminum (Alq_3), as an emissive layer and also as an electron transport layer; lithium-aluminum alloy (LiAl), as a cathode, respectively.

Devices were fabricated on the ITO coated glass which is purchased from the Samsung Corning Precision Glass. Before using the ITO coated glass, it was finely cleaned by ultrasonication with organic solvents and deionized water. The active area of the device is 5×5 mm^2. The organic, inorganic and cathode layers were subsequently deposited by thermal evaporator at a base pressure of about 10^{-6} Torr. The deposition rate of all organic materials were ~1 Å/s.

In order to find out the influence of ITO surface modification by plasma treatments, thin films of CuPc were deposited by the thermal evaporation on the finely cleaned ITO coated glass substrates. The ITO coated glass substrates were treated with plasma like the OLED before the thin films of CuPc were deposited on it. The surface morphology of the CuPc thin films on ITO surfaces has been studied using the MultiMode V (Veeco Instruments, Inc.) scanning probe microscope (SPM) with TappingMode™.

The electroluminescence (EL) was measured using the PR-670 SpectraScan Spectroradiometer (Photo Research, Inc.) and the Model 237 High-Voltage Source-Measure Unit (Keithley Instruments, Inc.). The devices were measured in dark box and air atmosphere.

3. Results and discussion

Fig. 2 shows the SPM images of the CuPc thin films on the ITO substrates treated with different plasma. The roughness and phase of CuPc thin films have been affected by the plasma treatments. Table 1 summarizes the root mean square (RMS) value of the surface roughness and phase of the CuPc thin films. The roughness remarkably depended on the plasma treatments in order of CF_4-P>untreated control>O_2-P. Also the phase shows the similar tendency in order of CF_4-P>untreated control>O_2-P. It has been reported that the surface energy and polarity of substrates significantly influences the growth of organic molecular which is deposited on the substrate [4–5,7–8]. The reduced polarity by the CF_4-P affected the growth of CuPc thin films to be more crystalline, and the striation of protrusions suggests their crystalline nature [9].

Figs. 3–5 shows the EL characteristics of fabricated OLEDs having the plasma treated ITOs. The O_2-P treated OLED showed the reduced turn-on voltage than an untreated bare control device. This driving voltage drop could have been caused by the enhanced carrier injection from the reduced hole-injection barrier. In the case of the CF_4-P

Table 1
Summarize of the surface morphological study of CuPc thin films.

Samples	Results of scanning probe microscope	
	Roughness (RMS)	Phase (RMS)
Control-untreated	26.6 nm	11.3°
CF_4-P	30.5 nm	24.4°
O_2-P	25.4 nm	10.2°

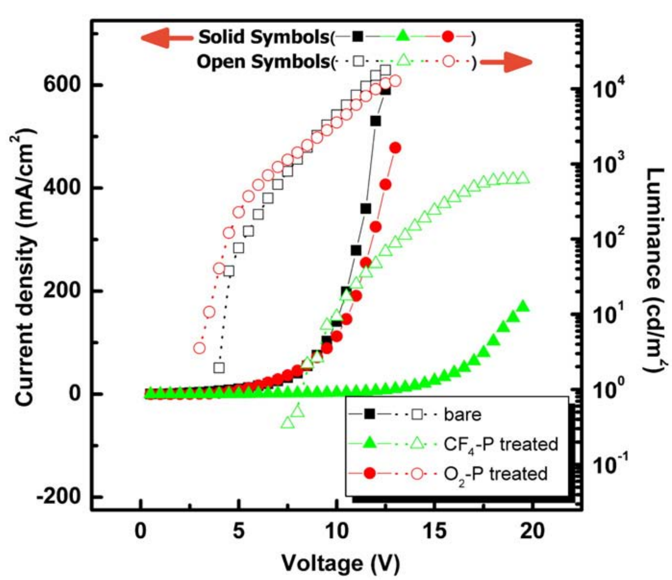

Fig. 3. The current density and the luminance characteristics as a function of the applied voltage.

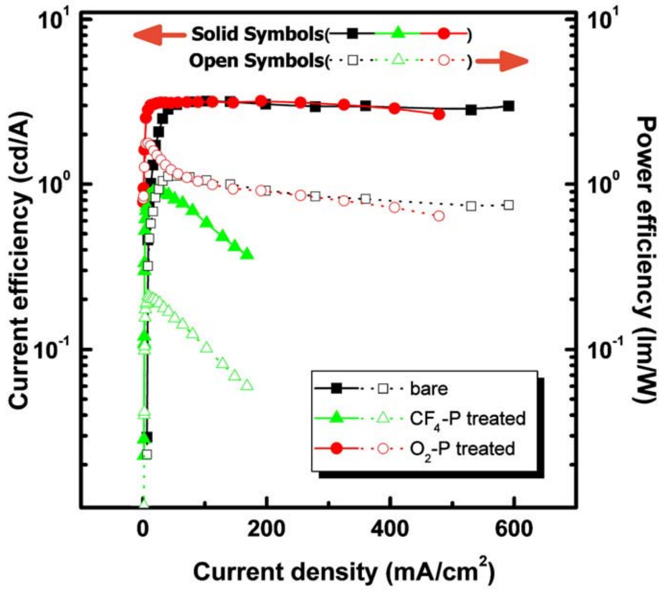

Fig. 4. The current efficiency and power efficiency characteristics of the OLEDs as a function of the current density.

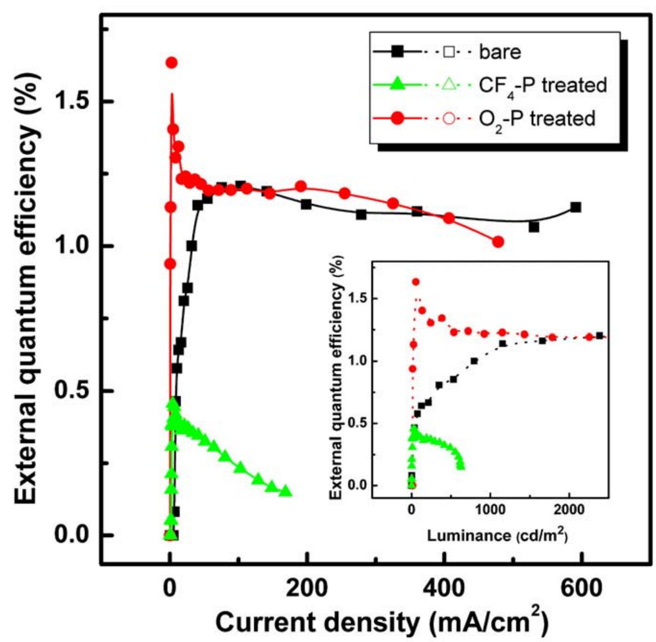

Fig. 5. The external quantum efficiency characteristic (EQE) the OLEDs as a function of the current density. The inset is a magnified view of EQE as a function of luminance.

treated OLED, the driving voltage was significantly increased, and also the luminance was significantly decreased. This result is different from the previous studies which reported that the CF_4-P treated OLED had improved performances [3,5]. The ineffectiveness of CF_4-P treatment could be seen in Figs. 4 and 5, also. While the current efficiency and power efficiency of O_2-P treated OLED dramatically increased in low current density region, that of the CF_4-P treated OLED significantly decreased in low current density region. The dependence of plasma treatment was not different from the previous reports when the O_2-P was used. The external quantum efficiencies of OLEDs were 1.4%, 0.6%, and 0.4% at 100 cd/m^2 in order of O_2-P, control, and CF_4-P. These results are due to the dependence of CuPc growth on the polarity of ITO surface. As F. Yang, et al. [9] reported, the growth of CuPc is significantly affected by the deposition condition. Moreover the growth of the CuPc significantly depended on the polarity of ITO surface. And the OLED with CuPc HIL showed the different tendency from the previously reported plasma treated OLEDs. Under the nature of CuPc protrusions, the shadowing effect by the protrusions is expected. As a result, the overall coverage of CuPc/NPB interface decrease, and the OLEDs show a drop in EL characteristics. The increased surface roughness and phase, and EL characteristics of OLEDs support the above explanations.

4. Conclusion

The EL characteristics of the OLEDs with plasma treated ITO anode electrode depended on the kind of organic materials used for the HIL or HTL. When the CuPc was used to the HIL, the CF_4-P treatment was not adequate due to the depending tendency of CuPc growth on surface polarity, while the O_2-P treatment was still a promising technique. The growth modes of organic materials are affected by the surface condition parameters in different ways; such as surface energy, polarity. The kind of the interfaced organic material with the ITO anode electrode is important in determining which plasma treatment is adequate. The change of the growth mode of HIL material is also important as much as the work function shift of ITO anode electrode and this change significantly affects the performance of OLED.

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