Properties of Polymer Light-Emitting Diodes Coated on Surface-Treated ITO/Glass Substrates

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ABSTRACT: We fabricated blue polymer light-emitting diodes (PLEDs) with indium tin oxide (ITO)/PEDOT : PSS/PVK/PFO-poss/LiF/Al structures. All of the organic film layers were prepared by the spin-coating method on plasma and heat-treated ITO/glass substrates. The dependences of the optical and electrical properties of the PLEDs on the plasma and heat treatment of the ITO film and the introduction of poly(*N*-vinylcarbazole) (PVK) layer were investigated. The AFM measurements indicated that the surface roughness of the ITO transparent film was improved by the plasma and heat treatment. In the emission spectra, the intensity of the excimer peaks of the PFO-poss [polyhedral oligomeric silsesquioxane-terminated poly(9,9-dioctylfluorene)] emission layer were decreased for the PLED device with the PVK film layer compared with the one without the PVK layer. The maximum current density, luminance and current efficiency of the PLEDs were found to be about 470 mA/cm^2, 486 cd/m^2 at an input voltage of 12 V and 0.55 cd/A at 100 cd/m^2 in luminance, respectively. The color coordinates (CIE chart) of the blue PLEDs were in the range of $x = 0.17 \sim 0.20$, $y = 0.13 \sim 0.16$, and the peak emission spectrum was about 430 nm, showing a good blue color. J Appl Polym Sci 110: 3678–3682, 2008

Key words: polymer light-emitting diode; blue color; PVK; PFO-poss; luminance; O_2 plasma treatment; ITO film

INTRODUCTION

Recently, polymer light-emitting diodes (PLEDs) have attracted much attention for applications in large size flexible displays[1–3] because of their simple structure and facile fabrication using soluble coating methods[4,5] (spin coating or ink-jet printing). The PLED is the current operational device which emits light through the recombination of excitons injected from the anode and cathode electrodes. It is desirable to prepare PLEDs with good interfacial adhesion properties and surface morphology between the electrode and organic films.[6] In particular, to optimize the electron and hole recombination process at the emitting layer, it is necessary to carry out surface treatment of the indium tin oxide (ITO) electrode film and improve the adhesion between the interlayer films. It is established that the plasma treatment removes the impurities on the substrate and reduces the surface roughness of ITO electrode. Moreover, the plasma treatment increases the work function of ITO electrode and lowers the energy barrier for the injection of holes from anode.[7,8] Poly(*N*-vinylcarbazole) (PVK)[9,10] is often used as a hole injection and transport material in PLEDs.[11] Until now, many researchers have studied high-performance PLED devices. However, there are few articles describing the effects of the surface treatment of the ITO film and the introduction of a hole transport layer (HTL) on the electrical and optical properties of PLEDs. In this study, we prepared PLEDs with the structure of ITO/PEDOT : PSS/PVK/PFO-poss/LiF/Al using heat and plasma-treated ITO/glass substrates. The effects of the surface treatment of the ITO films and the introduction of the PVK layer into the device on the properties of the PLEDs were studied.

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EXPERIMENTAL

Materials and devices

To improve the surface morphology of ITO transparent electrode film, we investigated the dependence of

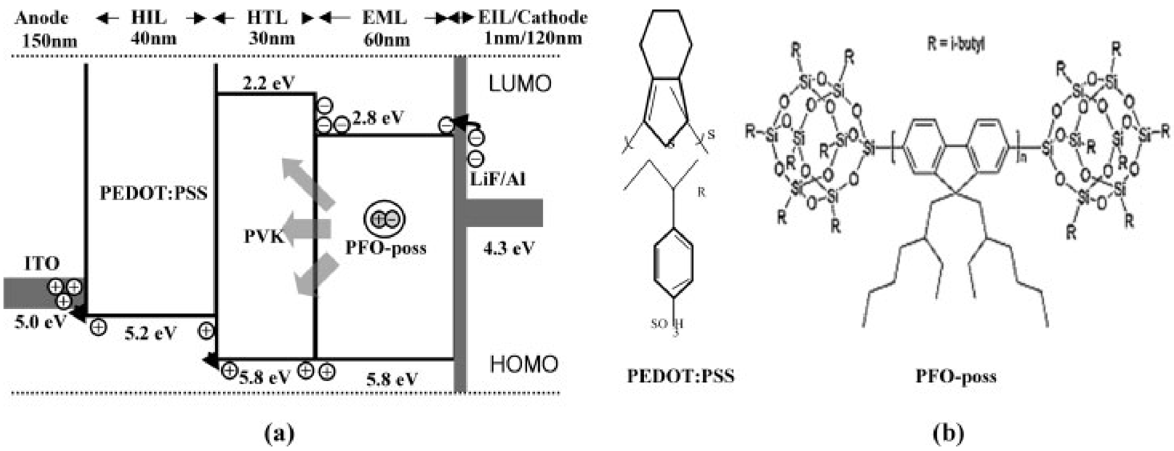

Figure 1 (a) the energy band diagram and (b) the structure of materials of the PLED device.

the electrical and optical properties of PLED devices on the surface treatments (plasma and low temperature annealing) of the ITO films. In addition, we studied the effect of the introduction of the PVK film layer into the PLED devices. For this, we prepared two kinds of samples with ITO/PEDOT : PSS/PFO-poss/LiF/Al (without PVK) and ITO/PEDOT : PSS/PVK/PFO-poss/LiF/Al (with PVK) structures.

Patterned ITO/glass was used as the substrate to prepare the PLEDS with the ITO/PEDOT : PSS/PVK/PFO-poss/LiF/Al structure.

To remove the organic particles, the substrates were cleaned using the SC-1 Process[12,13] (volume ratio of H_2O_2-NH_4OH-H_2O = 1 : 1 : 5) which was generally used semiconductor wafer process, followed by an ultrasonic precision cleaning process with acetone, isopropyl alcohol (IPA) and deionized water. The PEDOT : PSS [poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate][14–16] and PFO-poss [polyhedral oligomeric silsesquioxane-terminated poly(9,9-dioctylfluorene)][17–19] polymer materials used as the hole injection layer (HIL) and emission layers (EML) were coated on the substrates using the spin coating method. PEDOT : PSS was filtered through a 0.45 μm Milex filter and then spin coated on the substrate at 2000 rpm for 20 s. Then, the coated PEDOT : PSS film was dried at 100°C for 2 h in a vacuum oven. For the preparation of the multilayered PLED devices, the PVK used as hole transport layer (HTL) and PFO-poss polymer materials were dissolved in a mixture of 1 wt % mono-chlorobenzene and toluene. Following this, the prepared solution was spin coated onto the PEDOT : PSS/ITO/glass substrate at successive rotation speeds of 1000 rpm and 3000 rpm for 20 s each. These processes were carried out in a glove box under an N_2 gas atmosphere to protect the devices from moisture and oxygen. The film thicknesses of the PEDOT : PSS, PVK and PFO-poss layers were found to be about 40 nm, 30 nm, and 60 nm, respectively.

The LiF used as the electron injection layer and aluminum cathode electrode (LiF/Al) were deposited by the thermal evaporation method in a vacuum chamber with a base pressure of 5×10^{-8} Torr. The thicknesses of the LiF and Al films were about 1 and 120 nm, respectively.

The heat treatment of the ITO/glass substrate (Samples #2 and #3) was carried out at 180°C for 2 h in a vacuum oven. The conditions used for the O_2 plasma treatment of the ITO/glass substrate (Samples #1 and #3) were 100 W for 30 s in an RF plasma under O_2 at a pressure of 40 mTorr. The energy band diagram and structure of materials of the PLED device is shown in Figure 1(a,b).

Measurements

The surface morphology and roughness of the coated films were measured by Digital Instruments (Dimension 3100-IVa) atomic force microscopes (AFM). The AFM quantitative surface analysis with resolution in the nanometer region in all three dimensions is possible. In this experiment, the silicon cantilevers integrated tip of 125 μm length, and resonant frequency of 300 kHz were used for tapping mode imaging. The electrical properties of the PLEDs were investigated using an HP4145B semiconductor measurement system. For the measurements of the optical properties, luminance, spectrum wavelength, and CIE (Commission Internationale de I'Eclairage) color chart were evaluated using CS-1000 sprectro-radiometer (Konica Minolta).

RESULTS AND DISCUSSION

The plasma and heat-treatment effects of the ITO transparent films

Figure 2 shows the AFM morphologies of the ITO/glass substrates subjected to plasma treatment only

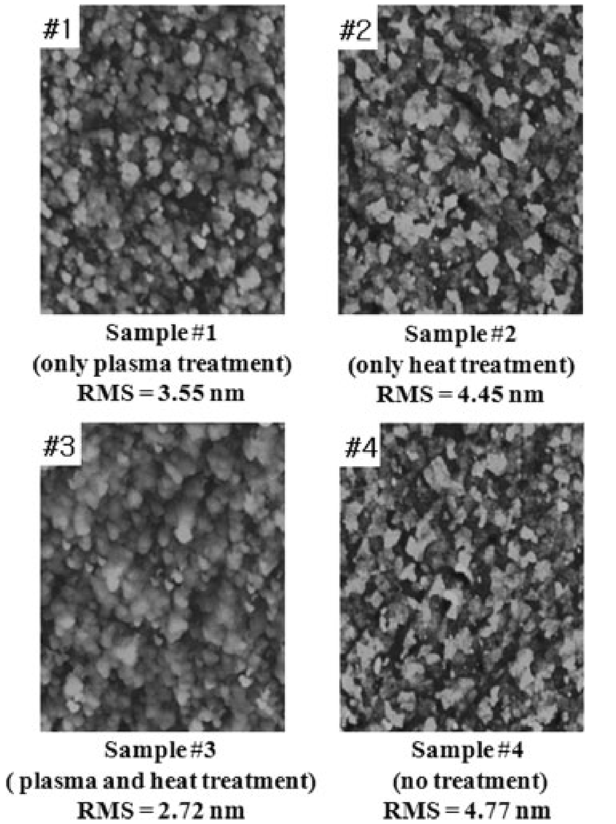

Figure 2 AFM surface morphologies of ITO films subjected to various surface treatments. (#1) only plasma treatment, (#2) only heat treatment, (#3) plasma and heat treatment, and (#4) no treatment.

(Sample #1), heat treatment only (Sample #2), both heat and plasma treatment (Sample #3), and without any surface treatment (Sample #4). The surface morphology of the ITO film without surface treatment (Sample #4) was relatively rough with the root means square (RMS) value of 4.77 nm and was improved by the plasma treatment (Sample #1), showing a lower RMS value of 3.55 nm. In addition, the RMS value of the ITO film was decreased to 2.72 nm when it was subjected to both plasma and heat treatment (Sample #3), showing the best surface roughness among the prepared ITO/glass substrates.

Figure 3 shows the current density versus voltage characteristics for the PLED devices coated on various ITO/glass substrate samples. The highest current density of 470 mA/cm^2 at 12V was obtained for the PLED sample coated on the plasma and heat-treated (Sample #3) ITO film. This result can be ascribed to the good surface morphology as well as the relatively low resistance of the ITO electrode film. In contrast, the PLED device coated on the ITO/glass substrate without surface treatment (Sample #4) showed the much lower current density of 356 mA/cm^2.

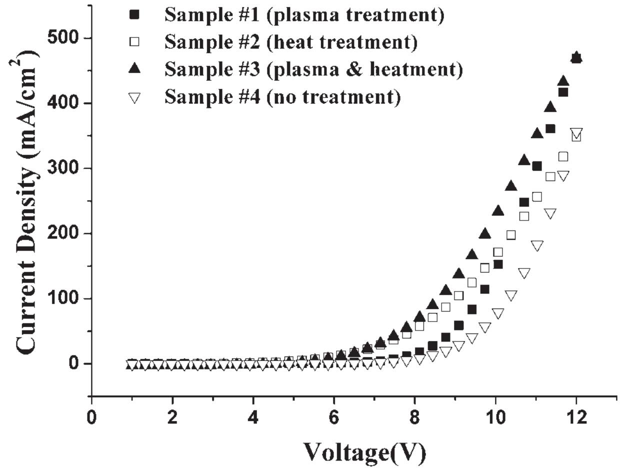

Figure 3 Current density versus voltage characteristics of the PLED devices coated on various surface treated ITO/glass substrates.

Figure 4 shows the luminance of the PLEDs coated on various ITO/glass substrates as a function of the applied voltage. The maximum luminance and current efficiency were found to be about 486 cd/m^2 (at 12 V) and 0.55 cd/A (at 100 cd/m^2), respectively, for the PLED device coated on the ITO film which was subjected to the plasma and heat treatment (Sample #3). From the AFM images of ITO films, and electrical, optical properties of PLEDs, we can conclude that the lowest values in the luminance and the current efficiency of the PLED coated on ITO/glass substrate without surface treatment may be due to higher sheet resistance and rough film surface of ITO electrode films.

The characteristics of the PLED devices at various surface treatment conditions of the ITO film are summarized in Table I. The emission spectrum peak was observed at about 430 nm, showing a good blue

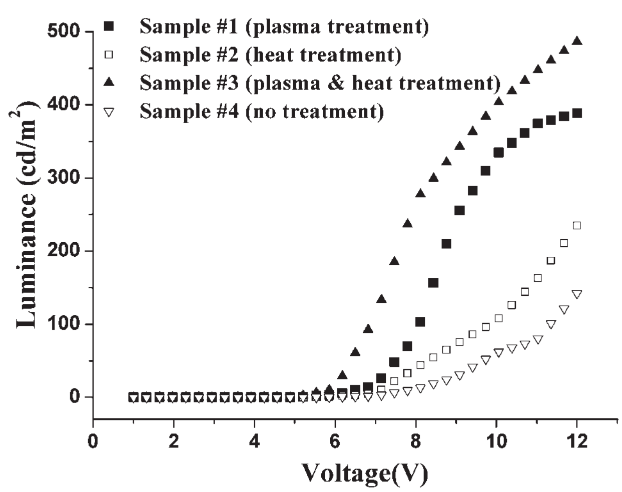

Figure 4 Luminance of PLED devices coated on various surface treated ITO/glass substrates as a function of applied voltages.

TABLE I
The Summary of PLED Device Characteristics at Various Surface Treatment Conditions of ITO Film

Sample number	Conditions Of ITO Surface treatment	RMS value (nm)	Current density at 12 V (mA/cm^2)	Luminance at 12 V (cd/m^2)	Current efficiency at 100 cd/m^2 (cd/A)
#1	Only O_2 plasma treatment	3.35	468	389	0.38
#2	Only heat treatment	4.45	349	235	0.08
#3	O_2 Plasma and heat treatment	2.72	470	486	0.55
#4	No treatment (bare)	4.77	356	142	0.04

color. The relatively low luminance of the PLED samples in this experiment may be caused by the fact that the prepared PLED devices were not subjected to any passivation treatment to protect them against air.

The effects of introducing the PVK layer

To investigate the effect of introducing PVK layer, the PLEDs with and without PVK layer were prepared, and the electrical and optical properties of the devices were compared. The luminance efficiency can be increased by introducing a PVK film layer into the PLED device because the PVK layer plays the role of a HTL as well as an electron blocking layer. This is due to the fact that the energy level of the lowest unoccupied molecular orbital (LUMO) of the PFO-poss emission layer can be reduced by 0.6 eV through the introduction of the PVK layer, which facilitates recombination of electrons and holes.

Figures 5 and 6 show the current density and luminance curves of the PLED devices with and without the PVK layer coated on the plasma and heat-treated ITO/glass substrates. The PLED device with the PVK layer showed a higher luminance compared with the one without the PVK film layer. The measurement of the current density showed similar results to the luminance properties of the PLED. That is, the current density of the PLED with the PVK layer was 470 mA/cm^2 and decreased to 402 mA/cm^2 at 12V for the PLED without the PVK layer. The maximum luminance for the PLED with and without PVK were found to be 486 cd/m^2 and 393 cd/m^2 at 12 V, respectively. This result is attributed to the introduction of the PVK layer, which is believed to increase the hole transport efficiency in the PFO-poss emission layer. Therefore, the hole transport and electron blocking functions of the PVK layer improve the recombination of the excitons in the emission layer, resulting in a good device performance. This can be also explained such that there is no energy barrier in highest occupied molecular orbital (HOMO) level between PVK and PFO-poss layer as shown in Figure 1(a).

Figure 7 shows the CIE chart of the PLED devices (a) with PVK and (b) without PVK layer. The CIE color coordinates of the PLEDs with and without PVK were $(x, y) = (0.19, 0.16)$ and $(x, y) = (0.22, 0.25)$, respectively, indicating that the emission color shifted from blue to greenish. In addition, the maximum peak wavelength of the PLED with PVK layer was found to be around 430 nm. There was a strong second peak at around 470 nm of the emission spectrum for the PLED without PVK layer. This color shift to longer wavelength for the device without

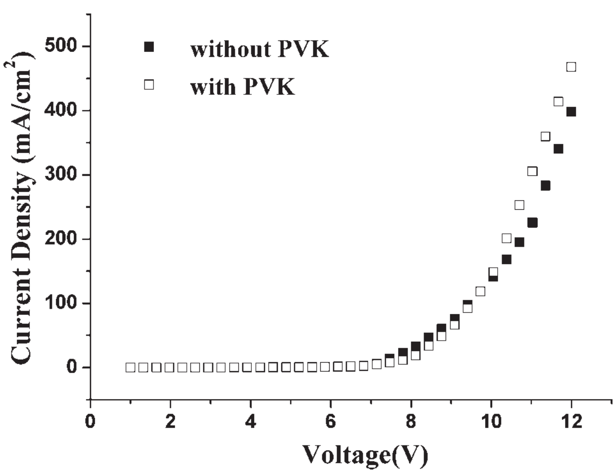

Figure 5 Current density versus voltage curves of the PLED devices with and without PVK layer.

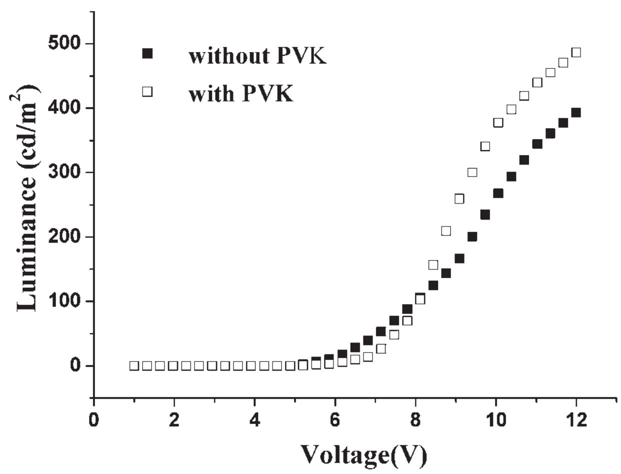

Figure 6 Luminance of the PLED devices with and without PVK layer as a function of applied voltages.

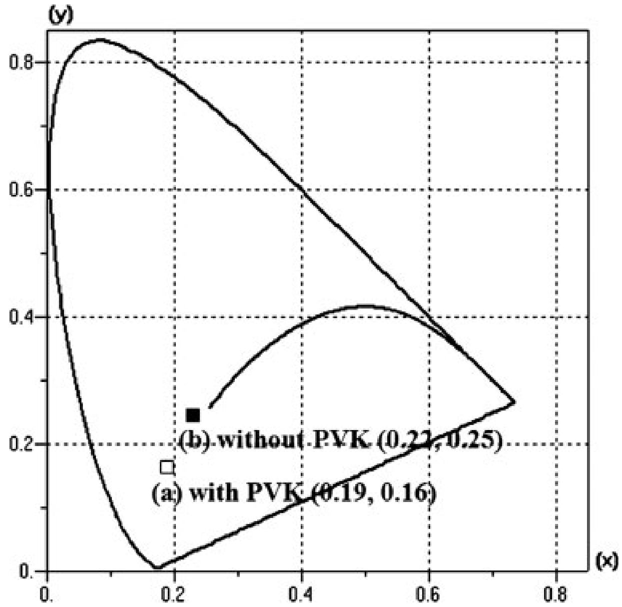

Figure 7 CIE chart of the PLED devices (a) with PVK and (b) without PVK layer.

PVK may be attributable to exciplex formation between the PFO-poss (EML) and PEDOT : PSS (HIL) due to the superposition of each absorption spectrum.[20]

CONCLUSIONS

PLED devices with the structure of ITO/PEDOT : PSS/PVK/PFO-poss/LiF/Al were prepared on various plasma and heat-treated ITO/glass substrates. The optimum surface treatment condition of the ITO/glass substrate was heat treatment at 180°C for 2 h followed by O_2 plasma treatment at an RF power of 100 W under O_2 at a pressure of 40 mTorr. The RMS value of the ITO film was decreased from 4.77 nm to 2.72 nm by the surface treatments of the O_2 plasma and low-temperature heating, leading to the improvement of the ITO surface roughness. The maximum luminance and light emission efficiency were 486 cd/m^2 (at 12 V) and 0.55 cd/A (at 100 cd/m^2), respectively. The luminance and current density were increased by the introduction of the PVK HTL into the PLED device. This may be related to the effective electron blocking and hole transportation of the PVK layer in the PFO-poss emission layer of the PLED device.

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