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Polymer Light-Emitting Diode Prepared by Floating-Off Film-Transfer Technique

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Floating-off film-transfer technique was used for the formation of semiconducting polymer multi-layers and the effect on the performance of polymer light-emitting diode (PLED) was studied. This method made it possible to avoid the solvent compatibility problem that was typically encountered in successive coating of polymeric multilayer by solution processing. F8BT and MEH-PPV were used for electron transporting layer (ETL) and for emissive layer, respectively. Current-voltage-luminance characteristics and luminescence efficiency results showed that the insertion of ETL by floating-off film-transfer technique followed by proper heat treatment resulted in a significant improvement in PLED operation due to its electron-transporting and hole-blocking abilities.

Keywords Polymer light-emitting diode; floating-off film transfer; heat treatment; Electron-transporting layer; F8BT; MEH-PPV

Introduction

Since the discovery of electroluminescence (EL) in conjugated molecules [1, 2], there has been remarkable progress in the commercialization of the technique. Comparing small molecular organic light-emitting diodes (OLED), polymer light-emitting diodes (PLED) have the advantages that they are easy to fabricate by convenient solution process and that they have excellent mechanical properties for the applications in displays and lights [3].

The recombination of holes and electrons, which generates the EL of the devices, is improved critically by making multilayered structure, where holes are injected and transported from one side of the layers, while electrons are injected and transported from the other [4–6]. For the small molecular OLED, the multilayered structures is made by consecutive sublimation, but the PLED in similar device architectures is difficult to obtain by consecutive wet processes. A conjugated polymer has similar solvent comparability in

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commonly used solvent, so that the interface damage at best and most likely dissolution of the underlying layer partially or completely restrict the subsequent processing steps. It is imperative for the integrity of the interface that the polymer in the first layer is not dissolved in the solvent used for the second layer. Several procedures were developed to solve this problem. A soluble precursor was used for the first layer and the precursor became insoluble by subsequent reaction such as cross-linking reaction [7, 8]. Double spin-coating process was tried by choosing the polymer that was insoluble in the second solution [9]. Floating film-transfer method has also been developed where the dissolved molecules could self-form a floating film on the liquid substrate after volatilization of the organic solvent [10, 11]. Still more fundamental approach is asked to research regarding fabricating multilayered PLED.

In this report, we presented a floating-off film-transfer technique, which has been used previously for studying the diffusion and compatibility of polymer films [12], for forming a double-layered polymeric semiconducting films. The electron transporting film was floated off onto a non-solvent surface (deionized water) and then the floating film was picked up with the polymeric emissive layer which had been already coated on the substrate. Thus, fabricated PLED was followed by appropriate annealing process. This technique may be able to open the door to exploring and utilizing various combinations of polymers in PLED that could not have been tried due to solvent compatibility problem.

Experimental Details

Polymers used were poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) and poly(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV), which were used as ETL and emissive layer respectively. These were purchased from Aldrich and used without further purification. The device structure and the energy levels of the molecules used were shown in Fig. 1(a) and (b). Considering the LUMO/HOMO levels of the molecules and electron transporting ability, F8BT was expected to facilitate the electron transport and the hole blocking (Fig. 1(b)) [13].

The multisemiconducting-layered samples for EL measurement were prepared as follows. Firstly, the hole collection electrode was prepared by spin-coating the polymer complex of poly(3,4-ethylenedioxythiophene) and poly(styrene-sulfonate) (PEDOT–PSS) on a cleaned ITO-glass substrate and thereafter annealing it at 135°C for 10 min (denoted as PEDOT-PSS/ITO-deposited glass film). Secondly, MEH-PPV was dissolved in xylene and a 70-nm-thick MEH-PPV layer was spun casted onto the above PEDOT-PSS/ITO-deposited glass film (denoted as MEH-PPV/PEDOT-PSS/ITO-deposited glass film). Thirdly, F8BT was dissolved in xylene and a 30-nm-thick F8BT polymer film was spun onto a silicon substrate which had been treated with piranha solution (a mixture of sulfuric acid and hydrogen peroxide) for gaining hydrophilic surface. Hydrophilicity of the silicon surface facilitated water to penetrate into the interface between F8BT layer and a silicon substrate, so that F8BT layer could be peeled off and floated onto the surface of deionized water (Fig. 2(a)). Fourthly, floating F8BT polymer film was picked up on MEH-PPV/PEDOT-PSS/ITO-deposited glass film (Fig. 2(b)). The resulting device was annealed at the temperature (160°C) above the glass transition temperatures (Tg) of the polymers for 30 min.

For comparison two more diodes were prepared: the one with the same structure as above but without annealing process, and the other with single 100-nm-thick MEH-PPV layer with the heat treatment. The total thickness was kept identical, and therefore electric

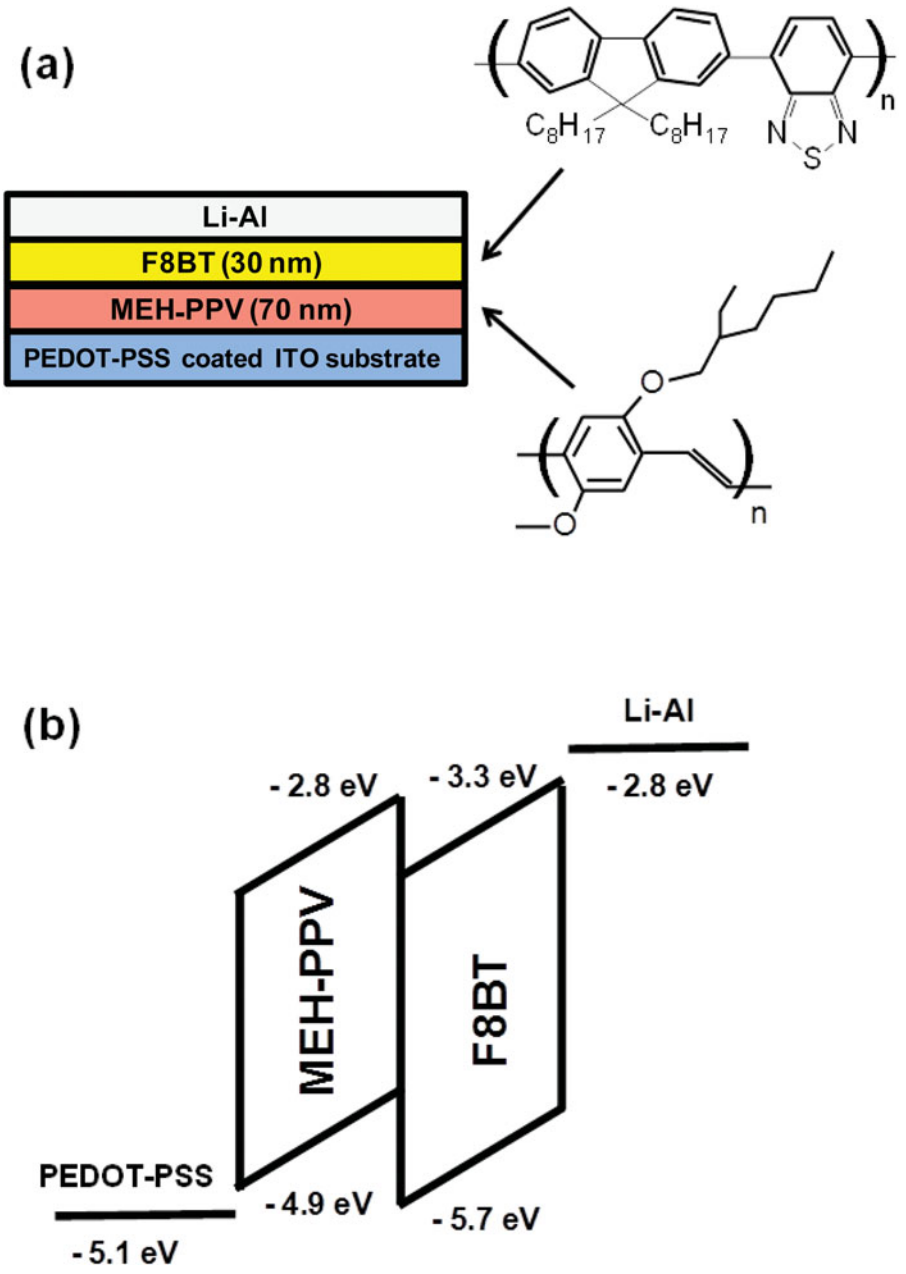

Figure 1. (a) Multilayered structure of PLED and molecular structures of MEH-PPV and F8BT, and (b) energy diagram of the multilayered PLED.

field within the device was made to be identical in all cases. The above processes were carried out under air atmosphere.

Lithium-aluminum alloy (60 nm) was finally vacuum-deposited on the top of the polymer active layers as an electron collecting electrode. The optical and electrical properties of the PLEDs, such as the current density, the EL, and the emission spectra were measured

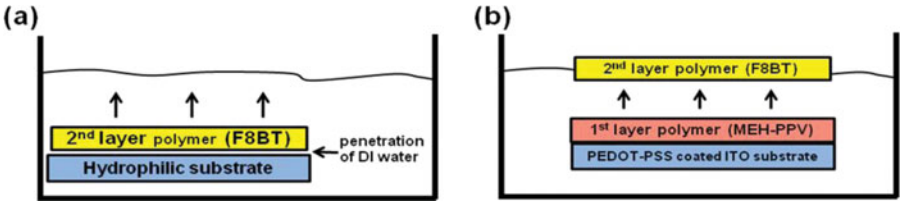

Figure 2. A schematic of floating-off process for fabrication of bilayered PLED. (a) F8BT layer could be peeled off and floated onto the surface of deionized water, and (b) floating F8BT polymer film was picked up on MEH-PPV/PEDOT-PSS/ITO-deposited glass film.

with Keithley 236 and CS-1000A instruments. All the measurements were carried out under ambient conditions at room temperature.

Results and Discussions

Treating silicon substrate with piranha solution made the surface more hydrophilic and facilitated water to penetrate into the interface between F8BT layer and a silicon substrate, so that F8BT layer could be easily peeled off and floated onto the surface of water bath. The devices with semiconducting polymer multilayers could be successfully fabricated for studying the effect of the inserted ETL and of the proper heat treatment on the performance of thus prepared PLED.

EL spectra of ITO/PEDOT-PSS/MEH-PPV/Li-Al and ITO/PEDOT-PSS/MEH-PPV/F8BT/Li-Al(annealed at 160°C for 30 min) were shown in Fig. 3. Each device was maintained under constant forward bias, and their emission was recorded. The resulting red emission of the devices was exclusively from the EL of the MEH-PPV layer and F8BT layer serves as ETL [14–16]. Comparing the EL spectra of MEH-PPV-only device (denoted as "a"), electrical excitation of the bilayer device showed the red-shifted emission (center at

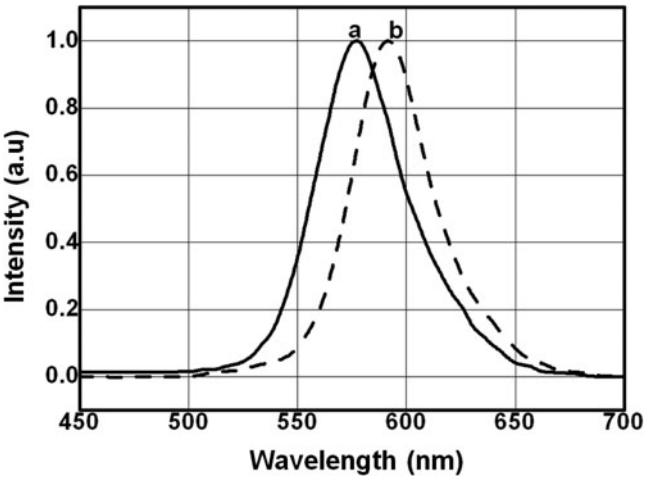

Figure 3. Normalized EL spectrum of single-layered and bilayered PLED: (a) the device with MEH-PPV single layer and (b) the device with MEH-PPV/F8BT bilayer(annealed at 160°C for 30 min).

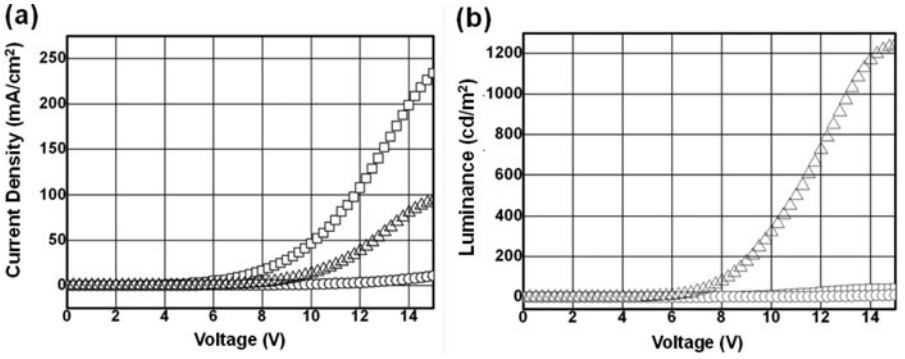

Figure 4. (a) The *I-V* characteristics, and (b) luminance characteristics of MEH-PPV single-layered PLED (□), MEH-PPV/F8BT bilayered PLED with heat-treatment (Δ) and without heat treatment (○).

~590 nm) presumably due to exciplex emission [17], while the F8BT emission was totally absent. This red-shifted EL peak indicates that the emission occurring near the interface was not from F8BT layer considering the larger band gap of F8BT than that of MEH-PPV [13, 17].

Figure 4 (a) and (b) showed the current density–voltage (I-V) and the luminance–voltage (L-V) results, respectively, of three-types of devices: (1) MEV-PPV single-layered device, (2) MEH-PPV/F8BT bilayered device with heat treatment, and (3) MEH-PPV/F8BT bilayered PLED without heat-treatment. The lower current of bilayered PLED, regardless of heat treatment, was caused by the deeper HOMO-level of F8BT (~0.8 eV difference) which limited hole injection. The heat treatment was performed in vacuum oven after floating-off process at 160°C, the temperature above the Tg's of MEH-PPV and F8BT to facilitate the conformal contact at the hetero-junction of two polymeric layers [12]. The heat treatment increased the current by 10 times.

The L-V curves of the three PLED's were shown in Fig. 4(b). The bi-layered device with heat-treatment (denoted as "△") showed the highest luminescence characteristic. This L-V curve proved that bilayered PLED fabricated by floating-off technique followed by heat treatment, was superior to the single-layered MEH-PPV device. It means that F8BT layer acted not only as electron transporting layer but also served as a hole blocking layer, resulting in efficient electron-hole recombination at the MEH-PPV/F8BT heterojunction [17–19].

Comparison of the double layered devices with and without heat treatment (denoted as Δ and ○) demonstrated the importance of heat treatment. The PLED (ITO/PEDOT-PSS/MEH-PPV/F8BT/Li-Al) with heat treatment emitted light by more than ~23 times (1200 cd/m^2) compared to the one with identical device structure prepared without heat treatment. Annealing at the temperatures below the T_g's of both MEH-PPV and F8BT could not results in this improved L-V characteristic (the data are not shown here). If polymeric multilayered device prepared by floating-off technique was not treated properly by thermal annealing, the contact at the interface was incomplete so that the charge transport and the recombination of the charges were inhibited.

We calculated the luminescence efficiency using the current and the luminescence data for the three devices, which was shown in Fig. 5. As expected, the bilayer PLED with heat treatment showed the best efficiency characteristic and this again verified the possibility of

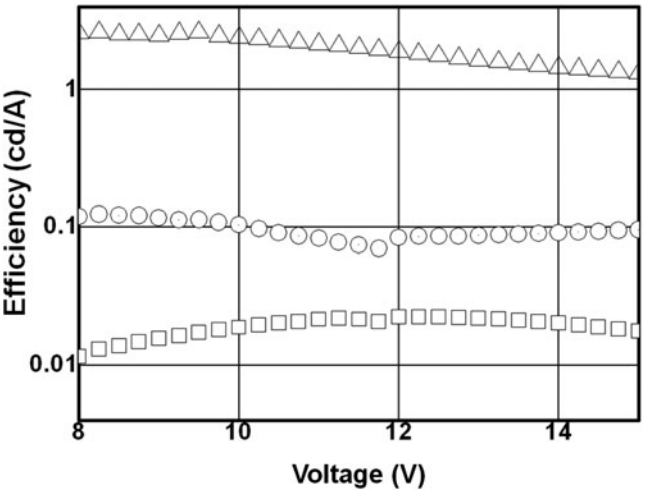

Figure 5. Efficiency characteristics of MEH-PPV single-layered PLED (□), MEH-PPV/F8BT bi-layered PLED with heat treatment (Δ) and without heat treatment (○).

floating-off technique for the application of multilayered PLED. It should be also addressed that the relatively low efficiency of our PLED is considered to be caused by the fact that the spin-coating processes and measurements were carried out under ambient condition, thereby possibly caused the oxidation of the semiconducting molecules to aromatic aldehydes [20].

Conclusions

In this study, we applied the floating-off technique to fabricated the device with the structure of ITO/PEDOT-PSS/MEH-PPV/F8BT/Li-Al. Comparing three cases, (1) the one without F8BT ETL layer, (2) the one with F8BT layer with heat treatment, and (3) the one with F8BT layer without heat treatment, the case (2) presents the best luminance (1200 cd/m^2) and luminance efficiency (0.18 lm/W). In conclusion, it was demonstrated that the floating-off film-transfer technique followed by appropriate heat treatment could be used to fabricate bilayered PLEDs.

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