Interfacial Engineering of Polymer Light Emitting Diode

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Abstract

The performance of polymer light emitting diode can be improved significantly by interfacial engineering on anode and/or cathode through adjusting the charge injection barriers for holes and electrons. Studies involve CFx and SAM modifications on ITO, thickness and delay time to baking of PEDOT:PSS, and electron injection/hole blocking layer.

1. Introduction

Polymeric light-emitting diodes (PLEDs) have drawn great attention in recent years because of their scientific importance and potentially commercial applications. However, the stability and performance of PLEDs are in needs of further improvement, resulting from imbalanced hole and electron fluxes and poor charge injection efficiency. Therefore, considerable efforts have been devoted to the studies on interfacial engineering for improving the device performance, which include modifications of indium tin oxide (ITO) surface, use of alkaline metal fluoride and inorganic salt as cathode, and incorporation of hole blocking/electron transport layer.

2. Results and discussion

A. Anode Modification and Hole Injection Layer Tuning

(1). Plasma-polymerization of CHF_3 on indium tin oxide surface as anode

For polymer light emitting diodes based on poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), we demonstrate that introducing a thin CF_x film formed by plasma polymerization of CHF_3 on an indium-tin oxide (ITO) anode surface to give the device, (ITO/CF_x/ MEH-PPV/Ca/Al), can lead to a high device performance (5.1 cd/A and 24 000 cd/m^2) (Fig. 1). The high device performance is attributed to a better balance between hole and electron fluxes, resulting from a formation of interfacial dipole at the CF_x/MEH-PPV interface, which provides a hole blocking effect and an enhancement of electron/hole recombination.

(2). Self-assembled monolayer (SAM) modification of indium-tin oxide anode surface

We demonstrate that introducing a self-assembled monolayer (SAM) derived from 1,1,1,3,3,3-hexamethyldisilazane (HMDS) on ITO anode surface for the device, ITO/SAM/ MEH-PPV/Ca/Al, can lead to an improvement in maximum device efficiency from 2.0 to 3.9 cd/A and maximum brightness from 33,000 to 34,400 cd/m^2 (Fig. 2). Such improvement is even better than that with introducing a layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) (2.6 cd/A and 16,000 cd/m^2), which is usually used as a hole transport (or injection) layer. The improvement results from a hole blocking effect and better wetting by converting the ITO surface from hydrophilic to hydrophobic provided by the SAM.

(3). Fine tuning hole injection via deposition of CF_x layer with proper ionization potential on indium tin oxide

For poly(9,9-dioctylfluorene) (PFO)-based light-emitting diodes, we demonstrate that by plasma polymerization of CHF_3 on an indium-tin oxide surface using various radio frequency powers for can control the extent of enhancement in hole injection resulting from a tuning of ionization potential of the anode. At the radio frequence power of 35 W, performance of the device, ITO/CF_x(35 W)/PFO/CsF/Ca/Al (Fig. 3), is optimal having the maximum current efficiency 3.1 cd/A and maximum brightness 8 400 cd/m^2. This is attributed to a better balance between hole and electron fluxes, resulting from a decrease in hole injection barrier provided by ultraviolet photoelectron spectroscopy (UPS) and scanning surface potential microscopy.

(4). Effect of thickness of PEDOT-PSS film on hole-injection barrier

The hole-injection barriers of PFO layer (1~10 nm) on the polymer electrode, PEDOT:PSS (on ITO) with various thicknesses have been measured by Ultraviolet Photoelectron Spectroscopy (UPS). The hole injection barrier height from PEDOT:PSS to PFO in the PFO-based light emitting diodes at the minimum thickness of PEDOT:PSS (15 nm) is the lowest among all due to the smallest extent of doping by residual PSS chains, as confirmed by the highest hole current of hole-dominated devices (Fig. 4). The occurrence of doping is supported by the broadening of the HOMO edge peaks of the UPS spectra of PFO films on PEDOT:PSS, especially for the thinner PFO film on the thicker PEDOT:PSS layer.

(5). Effect of Ionization potential (IP) change of the polymer anode, PEDOT:PSS, on the performance of polymer light emitting diodes due to its reaction with indium tin oxide

PEDOT:PSS coated on ITO is usually used to facilitate hole injection in polymer light emitting diodes. It is formed by spin-coating followed with baking, however, delay time to baking after the spin-coating can lead to a decrease of its IP and thus affect the device performance. We used ultraviolet photoelectron spectroscopy (UPS) to investigate ionization potential (IP) changes of the PEDOT:PSS films and found that increasing delay time can increase hole injection barrier to emitting polymer. The IP change is attributed to dedoping of the PEDOT in PEDOT:PSS due to reaction of ITO with protons in PSS and those in doped PEDOT in a presence of water. To get good performance of bipolar device with PFO, PEDOT:PSS film should be baked right after spin-coating.

B. Electron Injection/Hole Blocking Layer

We demonstrate a dual-functional composite layers having superior hole blocking effect along with electron transport capability for the two electroluminescent polymers, PFO and MEH-PPV. In addition, the composite cathode Cs_2CO_3/Ca is also introduced, which can enhance the electron injection dramatically. As a result, the PFO device has the performance with maximum brightness (B_{max}) 27 000 cd/m^2, maximum current efficiency (η_{max}) 3.5 cd/A, and pure blue emission with $CIE_{x,y}$ (0.16, 0.07). And the MEH-PPV device provides B_{max} 62 000 cd/m^2 and η_{max} 5.7 cd/A. To the best of our knowledge, these devices performances are the bset among those reported PLEDs using PFO or MEH-PPV as the emitting layer.

3. Summary

The performance of polymer light emitting diode can be improved significantly by interfacial engineering on anode and/or cathode through adjusting the charge injection barriers for holes and electrons.

4. References

1. C. C. Hsiao, C. H. Chang, M. C. Hung, N. J. Yang, and S. A. Chen, Appl. Phys. Lett., 86, 223505 (2005).
2. C. C. Hsiao, C. H. Chang, T. H. Jen, M. C. Hung, and S. A. Chen, Appl. Phys. Lett., 88, 033512 (2006).
3. C. C. Hsiao, C. H. Chang, H. H. Lu, and S. A. Cheng, Organic Electronics, **8**, 343-348 (2007).
4. C.-H. Chang, J.-L. Liao, M.-C. Hung, and S.-A. Chen, Appl. Phys. Lett., 90, 063506 (2007).
5. C.-H. Chang and S.-A. Chen, Appl. Phys. Lett., in press (2007).

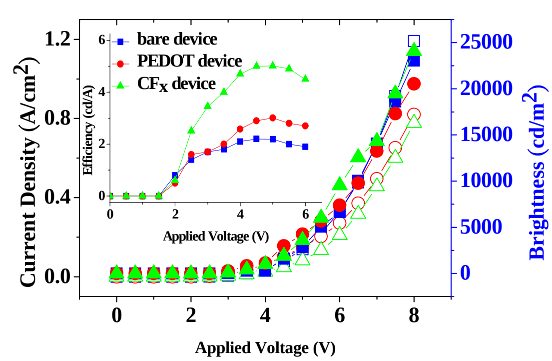

Figure 1. Current density-applied voltage-brightness curves for the bare, PEDOT, and CF_x devices. The close and open symbols are for brightness and current density, respectively. Brightnesses of the bare, PEDOT, and CF_x devices are ■, ●, and ▲, and the corresponding current densities are □, ○, and △, respectively. The inset is efficiency-applied voltage curves.

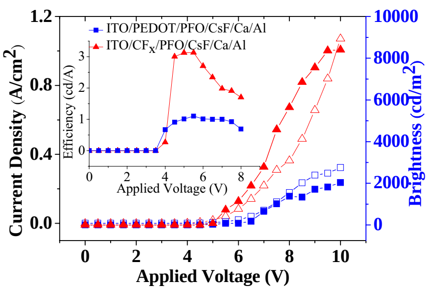

Figure 2. Current density-applied voltage-brightness curves for the bare-device, SAM-modified device, and PEDOT-device, the close and open symbols are for brightness and current density, respectively. Brightnesses of bare-, PEDOT-, and SAM-modified devices are ▲, ●, and ■, respectively. Current densities of bare-, PEDOT-, and SAM-modified devices are △, ○, and □, respectively. The inset is efficiency-applied voltage curves.

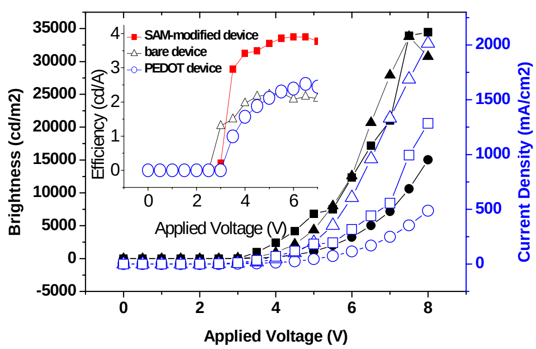

Figure 3. Current density-applied voltage-brightness curves for the devices, ITO/PEDOT/PFO/CsF/Ca/Al and ITO/CF$_x$(35 W)/PFO/CsF/Ca/Al; the close and open symbols are for brightness and current density, respectively. Brightnesses and current densities of the devices, ITO/PEDOT/PFO/CsF/Ca/Al and ITO/CF$_x$(35 W)/PFO/CsF/Ca/Al are ■, ▲, □, and Δ, respectively. The inset is efficiency-applied voltage curves.

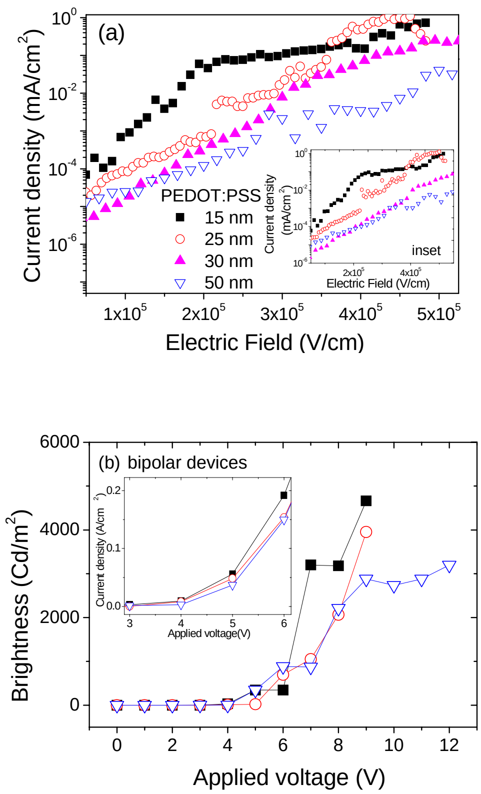

Fig. 4. **(a)** Hole-dominated devices (ITO/PEDOT:PSS/PFO (150 nm)/Au (3 nm)/Al) with different PEDOT:PSS thicknesses. PEDOT:PSS is taken as the anode and in the inset ITO is taken as the anode. **(b)** The performance of the bipolar devices ITO/PEDOT:PSS/PFO (100 nm)/CsF/Ca/Al with the three different PEDOT:PSS film thicknesses (15, 25, and 50 nm).