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Polymer light-emitting devices using poly(ethylene oxide) as an electron injecting layer

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The performance of polymer light emitting devices (PLEDs) based on polyvinyl carbazole (PVK) is improved by introducing a nanoscale interfacial thin layer, made of poly(ethylene oxide) (PEO), between the calcium cathode and the PVK emissive layer. It is believed that the PEO layer plays a key role in enhancing the device performance. In comparison to the device with Ca/Al as the cathode, the performance of the PLED with PEO/Ca/Al cathode, including the driving voltage, luminance efficiency is significantly improved. These improvements are attributed to the introduction of a thin layer of PEO that can lower the interfacial barrier and facilitate electron injection.

Keywords: Polymer light emitting devices; Electron injection layer; Electroluminescence

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Polymer light-emitting diodes (PLEDs) have attracted much interest worldwide since their discovery by Friend and co-workers in 1990 [1]. Engineering of the polymer-electrode interfacial properties is crucial to achieve balanced hole and electron injection for high efficiency operations. Low work function metals, such as calcium or barium are widely used as a cathode to facilitate electron injection [2-8]. These metals are very sensitive to moisture and oxygen and form detrimental quenching sites at areas near the interface between the electroluminescent (EL) layer and the cathode. In addition, metal ions formed at the metal/organic interface tend to migrate into the EL layer, thus, affecting the long term stability of devices [9]. To circumvent these problems, it is desirable to use high work-function metals (such as Al, Ag, or Au) as the cathode because of their better environmental stability and the simplicity of their device fabrication. To improve electron injection from high-work-function metals into the emitting layer, numerous approaches have been attempted [10,11]. For example, by inserting a thin layer of lithium fluoride, or cesium fluoride, between Al and the light emitting layer, the electron-injection ability could be significantly improved [10-12]. It was shown by the Cao et al. that the insertion of organic surfactant molecules between Al and the EL polymer could improve device performance up to the level obtained by low-work function metal cathode [11]. Li et al. reported that

effective electron injection can be achieved by the insertion of an ultrathin aluminum oxide layer between the Al and the emitting layer [13]. Lee et al. reported that polystyrene sodium sulfonate inserted between MEH-PPV and Al significantly improves electron injection [14]. Guo et al. reported that high performance polymer and small molecule OLEDs with an organic oxide, poly(ethylene glycol) dimethyl ether (PEGDE). Because PEGDE can be evaporated at low temperature compared to other inorganic insulators and improves the device performance as much as the inorganic electron injection layers, it could be a good candidate for an organic electron injection layer [15-17]. In this study, the performance of PVK based PLEDs is improved by using PEO/Ca/Al cathode. When a thin PEO (5 nm) buffer layer is introduced between the PVK emissive layer and the Ca cathode, the driving voltage of the device is reduced and the light efficiency is enhanced.

Experimental details

The ITO coated glass with a sheet resistance of 25 ohm/cm was used for the anode for PLED fabrication. For the preparation of PLEDs, the ITO glass was cleaned sequentially in ultrasonic bath of isopropanol, acetone, and de-ionized water. Finally, the ITO glass was sonicated in deionization water and then blown dry with N_2 gas. The poly(styrenesulfonate)

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(PSS)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) was used as the hole transport layer (HTL). A 40 nm thick PEDOT:PSS was spin coated onto precleaned and UV-O³ treated ITO substrates. The PEDOT:PSS layer was first baked at 150°C for 30 min to remove residual water and then moved into a glovebox under N₂ filled environment. The electroluminescent (EL) polymer films (PVK) was spin coated from solution to form different thickness on top of the PEDOT:PSS layer. The sample was baked at 60°C for 30 min to remove the residual solvent. Finally a PEO(5 nm)/Ca(60 nm)/Al(200 nm) thick metal cathode film was thermally deposited through a shadow mask to form top electrode in a vacuum of 1×10⁻⁶ Torr. EL spectra and CIE coordination of the devices were measured by PR650 spectra scan spectrometer and the current-voltage-brightness characteristics were simultaneously measured by a Keithley 2400 programmable voltage-current source. All the measurements were carried out at room temperature under ambient conditions. Figure 1 shows the device structure used in this study. The active emissive area of the device is 6 mm^2 .



FIG. 1 Schematic diagram of our PLED structure.

Results and Discussion

Figure 2 shows the current-voltage (I-V) characteristics of the different concentration of PVK. It was found that the 1 wt% device showed better performance compared to those of devices 2 wt% and 3 wt%. The turn-on voltage (7V) is the best for the device with 1 wt%. However for the other two (2 wt% and 3 wt%) PLEDs did not emit light. LUMO of Ca is -2.9 eV and LUMO of PVK is -2.3 eV, so it has a very high barrier for electron hopping. It will lead to the unbalance of electrons and holes. The electrons can not normally be injected from cathode



FIG. 2. Current-Voltage characteristics of the device with configuration of ITO/PEDOT:PSS/PVK/Ca/Al.

to emitting layer, due to the high energy barrier between them. Therefore we used the electron injection layer poly ethylene oxide (PEO) [18-20]. We have inserted the electron injection layer between cathode and the emitting layer by thermal evaporation.

Figure 3(a) shows the I-V curves for the devices made using PEO/Ca/Al as the cathode at various spin casting speeds of the PVK layer. The turn-on voltage decreased with increasing spin speed. The best spin speed and turn-on voltage were at 4000 rpm and 4.9 V. The turn-on voltage was reduced as the PVK film thickness decreased. The turn-on voltage at 2000 rpm and 3000 rpm were 6.5 V and 5.5 V, respectively.



FIG. 3. (a) Current-Voltage; (b) Brightness-Voltage characteristics of PLEDs with different spin-speeds, the device configuration is ITO/PEDOT: PSS/PVK/PEO/Ca/Al.

The brightness versus (L-V) voltage characteristics were shown in Fig. 3(b). The maximal luminance at 2000 rpm spin speed was 382 cd/m^2 . However, the maximal luminance at 3000 rpm and 4000 rpm were 234 cd/m^2 and 126 cd/m^2 , respectively.

Figure 4 shows the typical relationship among luminance efficiency, and current of PVK(1wt%) deposited at different spin speeds of 2000, 3000 and 4000 rpm for the polymer light emitting devices which exhibit maximum luminance efficiency of 0.105 cd/A, 0.094 cd/A, and 0.00445 cd/A respectively. The device with a concentration of 1wt% PVK and with a spin speed of 2000 rpm showed better properties. The normalized electroluminescence as a function of the emission wavelength of PLEDs with different spin speeds of PVK is shown in Fig. 5(b). Electroluminescence intensity produced by the devices is increasing with the decreasing spin speed of the PVK layer. There were three peaks at 440, 480 and 600 nm in Fig. 5(b). The PL spectrum of PVK showed only one peak at 410 nm (see Fig. 5(a)), but its EL spectrum showed three peaks. The first

peak was generated from intra-chain transition, and the other peak was generated from inter-chain transition.

The detailed device characteristics of the devices with different cathodes are summarized in Table I. For the device with Al cathode, a large turn-on voltage is needed to achieve a luminance of 1 cd/m^2 . However, when a Ca/Al layer cathode is used, the turn-on voltages of the device are reduced in comparison with Al device. Most importantly, as the device with PEO/Ca/Al cathode is used, the turn-on voltage is greatly reduced in comparison with Al and Ca/Al devices.

The insertion of PEO layer could increase performance as compared to Ca/Al and PEO/Ca/Al devices. Because the electron could hardly get injected from Ca to PVK, the addition of PEO between emitting layer and cathode layer could improve this condition. However, the insertion of PEO could let electrons inject to emitting layer. The electrons in emitting layer were increased. The recombination of electron-hole pair in PVK leads to emission of light. The device performance was enhanced by placing a monolayer of PEO at the contact interface between EL layer and the cathode, into the EL polymer layer [19]. In spite of the bulk resistance and the barrier height of PEO being much higher than that of the EL layer, the higher luminescence intensity and efficiency of devices suggest the injection of minority carriers (electrons) to be enhanced in their device configuration.

Conclusions

In summary, we have investigated the polymer light emitting diodes by using a PEO nanoscale interfacial layer to modify the cathode interface. It is found that the PLED could emit light and improve efficiency. Because electron injection function was increased by inserting PEO, the electron and hole were balanced in emitting layer. The electron-hole pair was





FIG.4. EL efficiency-current characteristics of the devices with different spin speeds.

recombined in PVK layer and light was emitted. The turn-on voltage is about 6.5 V, the maximal luminance and luminance efficiency are 382 cd/m^2 , and 0.105 cd/A.

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FIG. 5. (a) PL spectra of PVK; (b) Normalized EL emission spectra of the devices with different spin speeds.

TABLE 1. Performance of PVK-based PLEDs made with different cathodes.

Cathode Structure	turn-on voltage	maximum luminance
	(V)	(cd/m ²)
Al	Large*	no light
Ca/Al	7	no light
PEO/Ca/A1	6.5	382

*Large means the voltage is beyond the range of measured equipment

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