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Fabrication of Multilayer Polymer Light-Emitting Diodes with a Spin Coated Hole Transport Layer and Stamp Transfer Printed Emitting Layer

CHUL WOONG JOO, SOON OK JEON, KYUNG SOO YOOK, AND JUN YEOB LEE

Department of Polymer Science and Engineering, Dankook University
Jukjeon-dong, Suji-gu, Yongin-si, Gyeonggi-do, Korea

High efficiency multilayer polymer light emitting diodes (PLEDs) were developed using a stamp transfer printing process. Light emitting polymers were stacked on the spin-coated polymeric hole transport layer by using a stamp transfer printing method. The light-emitting efficiency of PLEDs was improved by more than 60% by stacking the light emitting polymers on the hole transport polymers using the transfer printing process.

Keywords High efficiency; multilayer structure; stamp transfer printing

Introduction

Polymer light emitting diodes (PLEDs) have several advantages over small molecule organic light emitting diodes (OLEDs) such as a simple device structure, a simple process and low material consumption [1]. However, device performances of the PLEDs are not as good as those of small molecule OLEDs and they should be improved further for practical applications. In particular, the light-emitting efficiency and lifetime of the PLEDs have to be enhanced.

There have been many studies to improve the efficiency and lifetime of the PLEDs [2–11] and the most effective approach was to insert a hole transport layer between poly-(3,4-ethylenedioxythiophen); poly-(4-styrenesulfonate) (PEDOT:PSS) and an emitting layer. Kim *et al.* introduced a thin polymeric hole transport material on PEDOT:PSS and reported that the efficiency of PLEDs was improved due to electron blocking effect of the polymeric hole transport material [2]. It was proposed that an insoluble layer was generated at the interface between PEDOT:PSS and the hole transport layer and contributed to the improved efficiency of PLEDs. The use of crosslinkable polymer hole transport layer was also efficient to improve the efficiency of PLEDs [3–7]. However, these approaches require the hole transport materials which are not soluble in common aromatic solvents. Therefore, soluble

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Address correspondence to Prof. Jun Yeob Lee, Department of Polymer Science and Engineering, Dankook University, Jukjeon-dong, Suji-gu, Yongin, Gyeonggi 448-701, Korea. Tel.: (+82)31-8005-3585; Fax: (+82)31-8005-3585; E-mail: leej17@dankook.ac.kr

hole transport materials cannot be used in these structures. Therefore, a method has to be developed to take advantage of soluble hole transport materials.

As an approach to fabricate multilayer PLEDs using a soluble hole transport material, a transfer printing process was applied in this work. After spin coating of the hole transport material, the emitting layer was coated by a stamp transfer printing method. The transfer printing method is a kind of a dry patterning process and even soluble hole transport material can be used to fabricate multilayer PLEDs.

Experimental

Device structure of indium tin oxide (ITO, 150 nm)/polyethylene-3,4-dioxythiophene: polystyrenesulfonate (PEDOT:PSS, 60 nm)/poly(9,9′-dioctylfluorene-co-bis-N,N′-(4-ethoxycarbonylphenyl)-bis-N,N′-phenyl-benzidine (PFO-co-NEPB, 16 nm)/yellow emitting polymer (50 nm)/LiF/Al was used for the stamp transfer printed PLED. A single layer device of the yellow polymer without the PFO-co-NEPB was also prepared as a standard device by a spin coating process. The yellow emitting material was a polyphenylenevinylene (PPV) based super yellow® polymer from Merck. The super yellow® polymer is a copolymer of alkoxy substituted PPV and alkoxyphenyl substituted PPV. The PFO-co-NEPB was spin coated from a 0.3 wt% toluene solution at a thickness of 16 nm without baking. The yellow emitting layer was formed by the transfer printing method using a polydimethylsiloxane (PDMS) stamp. The PDMS stamp was fabricated by curing Sylgard® 184 from Dow Corning Co. at 95°C for 2 h. Second substrate for transfer printing was silicone (Si) substrate. The Si substrate was ultrasonically cleaned in isopropanol for 30 min. After cleaning of the Si substrate, the PPV yellow polymer was spin coated from a 0.3 wt% toluene solution on the Si substrate at a spin speed of 2000 rpm and then the spin coated polymer film was transferred from the Si substrate to PFO-co-NEPB coated substrate. The spin coated polymer film was separated from the Si substrate by pressing and detaching the PDMS stamp from the yellow film on the Si substrate. The PDMS stamp with the yellow polymer film was contacted with the PFO-co-NEPB spin coated substrate at 120°C for 10 s under pressure and the yellow polymer film was transferred from the PDMS to the PFO-co-NEPB substrate. After the transfer printing of the PPV, the PPV was thermally annealed at 150°C for 10 min. LiF/Al was deposited as a cathode and then the device was encapsulated with a CaO getter and a glass lid. Current density-voltage-luminance curves and electroluminescence (EL) spectra of the devices were obtained using Keithley 2400 source measurement unit and a CS 1000 spectrophotometer.

Results and Discussion

The stamp transfer printing process can be used as a film coating method instead of a common spin coating and it is suitable for fabricating a multilayer device structure because it is a dry patterning process. A solid film is transferred from a Si wafer to the PDMS and the solid polymer film can be transferred to ITO substrate with a polymer charge transport layer. Therefore, a multilayer device structure can be easily fabricated by the stamp transfer printing method.

Figure 1 shows the current density-voltage-luminance curves of the standard device and the stamp transfer printed device with the PFO-co-NEPB layer. The current density was high in the standard device without the PFO-co-NEPB and the

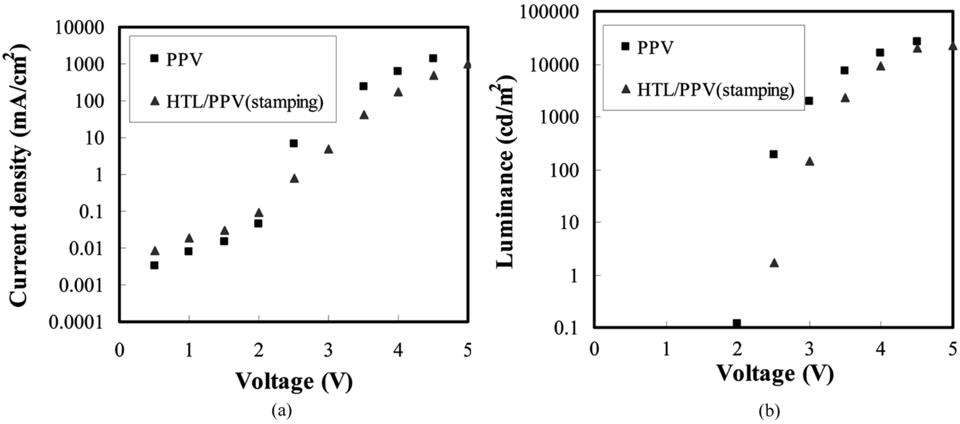

Figure 1. Current density-voltage-luminance curves of spin coated and stamp transfer printed yellow devices. (a) current density-voltage (b) luminance-voltage.

stamp transfer printed device showed lower current density than the standard device. The low current density in the device with the PFO-co-NEPB hole transport layer is due to the low hole mobility of the PFO-co-NEPB compared with that of the PEDOT-PSS. The PFO-co-NEPB has an aromatic amine structure and its mobility of $10^{-4}\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ order from time of flight measurements is lower than that of PEDOT-PSS which is doped with PSS p-type dopant. In addition, the energy barrier for hole injection between the PEDOT:PSS and the PFO-co-NEPB is also responsible for the low current density of the stamp transfer printed device with the PFO-co-NEPB. Energy level diagram of the stamp transfer printed device is shown in Figure 2. The luminance of the yellow devices followed the same tendency as the current density even though a relatively high luminance was obtained in the stamp transfer printed device with the PFO-co-NEPB. This may be due to the high recombination efficiency of the stamp transfer printed device with the PFO-co-NEPB hole transport layer.

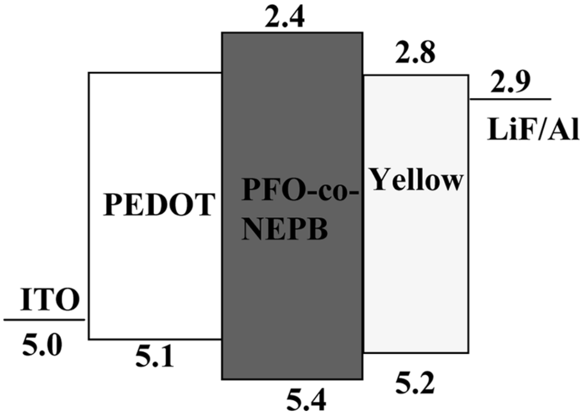

Figure 2. Energy level diagram of the polymer devices.

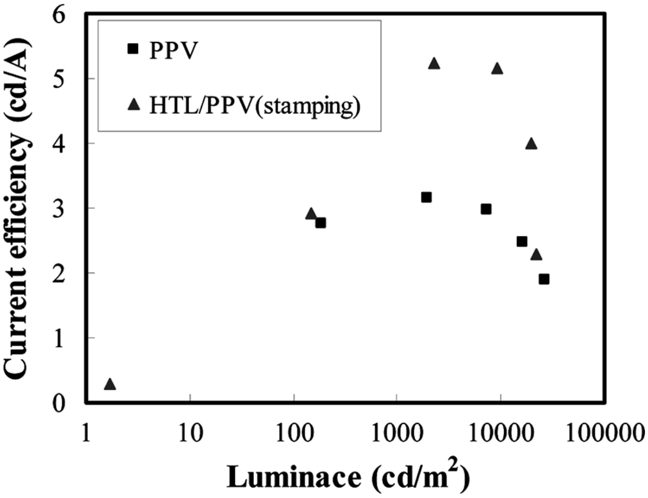

Figure 3. Current efficiency-luminance curves of spin coated and stamp transfer printed polymer devices.

The current efficiency of the yellow devices was plotted against luminance in Figure 3. A high current efficiency of 5.2 cd/A was obtained in the stamp transfer printed device with the PFO-co-NEPB, while a rather low current efficiency of 3.2 cd/A was observed in the device without the PFO-co-NEPB. The current efficiency was improved by more than 60% using the polymeric PFO-co-NEPB interlayer between the PEDOT-PSS and the yellow emitting layer. The improved current efficiency of the stamp transfer printed device with the PFO-co-NEPB can be explained by the electron blocking and reduced exciton quenching effect of the PFO-co-NEPB layer. It has been known that PEDOT-PSS can quench excitons in the polymer emitting layer due to free hole carriers in PEDOT-PSS [12]. Therefore, the efficiency is degraded in the device without the PFO-co-NEPB. The role of the PFO-co-NEPB is to separate the yellow light emitting layer from the PEDOT-PSS, suppressing the exciton quenching by the PEDOT-PSS. In addition, the lowest unoccupied molecular orbital (LUMO) of the PFO-co-NEPB is 2.4 eV and the LUMO level of the PFO-co-NEPB is suitable for efficient electron blocking. Therefore, the efficiency of the stamp transfer printed device was enhanced. The use of the stamp transfer printed process enabled the use of common polymer hole transport materials, resulting in increased efficiency in the polymer OLEDs.

EL spectra of the PPV devices with and without the PFO-co-NEPB layer are shown in Figure 4. Two devices showed almost the same EL spectra irrespective of the device structure, indicating that light emission is mostly come out of PPV emitting layer with little contribution of the PFO-co-NEPB and PEDOT-PSS layer in the two PPV devices.

Conclusions

In summary, a multilayer polymer OLED was effectively fabricated by a stamp transfer printing method. A light emitting polymer was coated on a spin coated polymeric hole transport layer by the stamp transfer printing process and the efficiency of

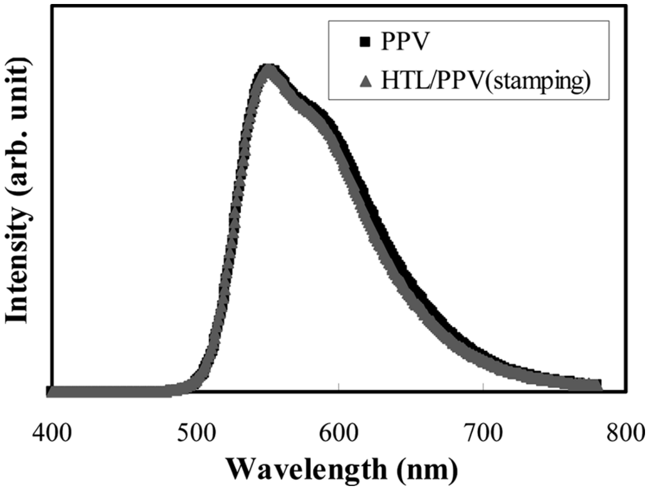

Figure 4. Electroluminescence spectra of spin coated and stamp transfer printed polymer devices.

the polymer OLED was improved by more than 60%. Based on this result, the stamp transfer printing method can be used as a low cost printing technology in organic electronic devices.

References

[1] Hebner, T. R., Wu, C. C., Marcy, D., Lu, M. H., & Sturm, J. C. (1998). *Appl. Phys. Lett.*, *72*, 519.

[2] Kim, J., Friend, R. H., Grizzi, I., & Burroughes, J. H. (2005). *Appl. Phys. Lett.*, *87*, 023506.

[3] Huang, Q., Cui, J., Yan, H., Veinot, J. G. C., & Marks, T. J. (2002). *Appl. Phys. Lett.*, *81*, 3528.

[4] Huang, Q., Cui, J., Veinot, J. G. C., Yan, H., & Marks, T. J. (2003). *Appl. Phys. Lett.*, *82*, 331.

[5] Yan, H., Lee, P., Armstrong, N. R., Graham, A., Evmenenko, G. A., Dutta, P., & Marks, T. J. (2005). *J. Am. Chem. Soc.*, *127*, 3172.

[6] Bernardo, G., Charas, A., Alcácer, L., & Morgado, J. (2007). *Appl. Phys. Lett.*, *91*, 063509.

[7] Bacher, A., Erdelen, C. E., Paulus, W., Ringsdorf, H., Schmidt, H.-W., & Schumacher, P. (1999). *Macromolecules*, *32*, 4551.

[8] Woo, S., Kim, J., Cho, G., Kim, K., Lyu, H., & Kim, Y. (2009). *J. Ind. Eng. Chem.*, *15*, 716.

[9] Kang, H. S., Park, K. N., Cho, Y. R., Park, D. W., & Choe, Y. (2009). *J. Ind. Eng. Chem.*, *15*, 752.

[10] Jeon, S. O., Yook, K. S., Joo, C. W., & Lee, J. Y. (2009). *J. Ind. Eng. Chem.*, *15*, 602.

[11] Yook, K. S., Jeon, S. O., Joo, C. W., & Lee, J. Y. (2009). *J. Ind. Eng. Chem.*, *15*, 420.

[12] Kim, J. S., Ho, P. K. H., Murphy, C. E., Seeley, A. J. A. B., Grizzi, I., Burroughes, J. H., & Friend, R. H. (2004). *Chem. Phys. Lett.*, *386*, 2.