Enhancement of Efficiency for White-Organic Light-Emitting Diode with a Thin Electron-Blocking Layer

Jung Soo Park,[a,b] **Joo Won Lee,**[a,b] **Young Min Kim,**[c] **Sung Jin Bae,**[c] **Jin Jang,**[b,*] **Jai Kyeong Kim,**[a] **and Byeong Kwon Ju**[c,z]

[a]*Opto-Electric Materials Research Center, Korea Institute of Science and Technology, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Korea*
[b]*Departments of Physics, Kyung Hee University, Seoul, Korea*
[c]*Department of Electrical Engineering, Korea University, Seoul, Korea*

In this study, we have enhanced the emission property of white-organic light-emitting diodes using the method of inserting the ultrathin electron-blocking layer (thin-EBL) between red–green–blue emissive layers. The devices into which three emissive layers are inserted were fabricated with indium tin oxide/CuPc/[N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine] (α-NPD/DPVBi/thin-EBL/Alq$_3$/Alq$_3$: 2 wt % 4-(dicyano-methylene)-2-methyl-6-(dimethylaminostyryl-4H-pyran (DCM1)/Alq$_3$/LiF:Al. To enhance the white emission property and improve the efficiency of devices, we suggest the α-NPD as the thin-EBL. According to knowledge of the energy band diagram, α-NPD was inserted between the blue-emitting layer and green-emitting layer. The α-NPD layer showed the effective blocking of electron as a function of thickness. From the Experimental, the effective blocking of electrons through controlling the thin-EBL thickness embodied the balanced white emission and improved the efficiency of the device. In our device with 0.3 nm α-NPD, it had a maximum power efficiency of 3.80 lm/W at 250 cd/m^2, a luminance efficiency of 5.14 cd/A at 4.83 mA/m^2, a luminance of 1200 cd/m^2 at 100 mA/cm^2, and the CIE coordinates were (0.353, 0.357), respectively.
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Because Tang and VanSlyke[1] reported highly efficient organic light emitting diodes (OLEDs) with a novel multilayer structure, many physical and chemical studies were continued as the next-generation flat panel displays. Because the application is possible from various displays with several advantages such as thinness, light weight, low driving voltage, fast response time, and the wide viewing angle. An advantage of OLEDs is that they are available in almost any wavelength in the vision region, and the spectrum design of white OLEDs is more flexible than for traditional discharge lamps where the available spectra depends on available phosphors and emissions from gas. From the information given above, white OLEDs will be able to embody large-area and full-color display, and they are also appealing as a high-quality and low-cost alternative for liquid crystal display (LCD) backlight and illumination light source. White is the most important color in the lighting industry. Thus, white OLEDs have attracted particular attention due to their potential. Because Kido et al.[2] obtained for the first time white OLEDs using a multiemitting layer device in which the three primary colors were emitted from different layers, white OLED performance continues to improve. A variety of methods have been proposed to achieve white emission. One approach is using a multilayer device in which three different color lights such as red, green, and blue are emitted from each layer and combined to give the white emission.[3-5] Another is the use of a complementary color relation.[6] The method which uses an additive mixture of three colors has a complicated fabrication process and structure. However, in the case where three colors radiate in balance, it will be able to realize the light which keeps all wavelengths in the visible region and be closer to the natural white light. Three-emitter (or more) white OLEDs are expected to provide good color rendering that can be used for general lighting. For applying white OLEDs to general illumination light sources, the white light must be required in a wide range of the visible spectrum with high efficiency, stability, high brightness, with CIE coordinates near (0.33, 0.33) through controlling the emission intensity for balanced emission.

In this study, we have fabricated white OLEDs using the conventional method of red–green–blue (RGB) stacked multilayers and improved the efficiencies of the devices. To obtain balanced white emission, the ultrathin electron-blocking layer (thin-EBL)

[N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine] (α-NPD), which forms the interfacial barrier for controlling electron blocking, was inserted between the emissive layers with knowledge of the energy band diagram.[7] In this work, by comparing the device performances with controlling α-NPD thickness, we found its optimum thickness. Then, the electron-blocking effect of α-NPD is directly observed in electroluminescence (EL) spectra and we can embody balanced white emission.

Experimental

The basic structure of the device configuration used in this study is shown in Fig. 1. Copper phthalocyanine (CuPc) was used as a hole injection layer (HIL), [N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine] (α-NPD) was used as a hole transporting layer (HTL) and an EBL, and 4,4′-bis(2,2′ diphenylvinyl)-1, 1′-biphenyl (DPVBi) was used as a blue-emitting material. Tris-(8-hydroxyquinoline) aluminum (Alq$_3$) was used as a green-emitting material and an electron-transporting layer (ETL). 2 wt % red-emitting 4-(dicyano-methylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM1)-doped tris-(8-hydroxyquinoline) aluminum (Alq$_3$) was used as a red-emitting material. The red-emitting layer was prepared by the simultaneous codeposition of DCM1 and Alq$_3$ evaporating from two separate heat-resisting crucibles. The optimal doping concentration for the red-emitting layer was determined to be 2 wt % for Alq$_3$.[8] The thickness of each emitting layer was controlled and confirmed. A bilayer of 1 nm lithium fluoride (LiF) and aluminum (Al) as an efficient cathode was deposited onto the organic film by vacuum evaporation.[9] Figure 2 shows the energy level diagram of a device where the thin-EBL (α-NPD) was inserted between the blue-light-emitting layer and green-light-emitting layer. The optimal thickness of each emitting layer was 7 nm, and we changed the thickness of the thin-EBL from 0.3 to 1 nm. EL devices were fabricated on indium tin oxide (ITO)-patterned glass plates (with a sheet resistance of 10 $\Omega/\square$) which were cleaned by sonication and then treated by oxygen plasma exposure.[10] All organic layers were thermally evaporated under a vacuum of 7×10^{-7} Torr with evaporation rates of around 0.1–0.15 nm/s, respectively. Film thickness was determined in situ using a crystal monitor. Light-emitting area was 10 $\times$ 10 mm. All of the device-performance measurements were carried out at room temperature in air without encapsulation. The devices were characterized by current density (J) vs applied voltage

Figure 1. The device structure.

Figure 3. The normalized EL spectra of the RGB stacked OLED under different thickness of each emitting layer.
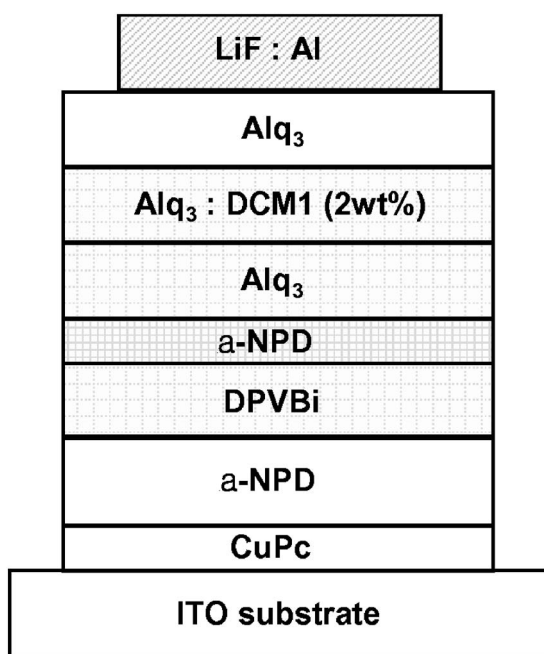
(V) and EL spectrum. The J-V characteristics of the device were measured by a high-voltage source-measure unit (Keithley, model 237, USA). EL spectrum was obtained with a pluorospectroscopy (ISS photon counter meter).

Results and Discussion

In our experiment, we analyzed the wavelength and CIE coordination of each monochrome device (RGB) before fabricating white OLEDs. EL peaks of blue, green, and red were observed at 460, 532, and 620 nm, respectively. Devices stacked with these RGB materials were constructed for white emission, and relative contribution of red, green, and blue emission can be controlled by changing the thickness of each emitting layer.[11] We fabricated devices with different thickness to find an optimized thickness of emitting layer. The thickness of each emitting layer was 15, 7, and 5 nm. From the Experimental section, the optimal thickness of each emitting layer was 7 nm, so the total thickness of three different emitting layers was 21 nm. Through the optimization of the thickness of all organic layers, white emission could be obtained with the CIE coordinates of (0.327, 0.353). The EL spectrum of RGB-stacked OLED is shown in Fig. 3. The EL spectrum showed a broad band covering the range of 400–700 nm. The red emission intensity was relatively weak compared to blue and green emission intensity, however. A greater
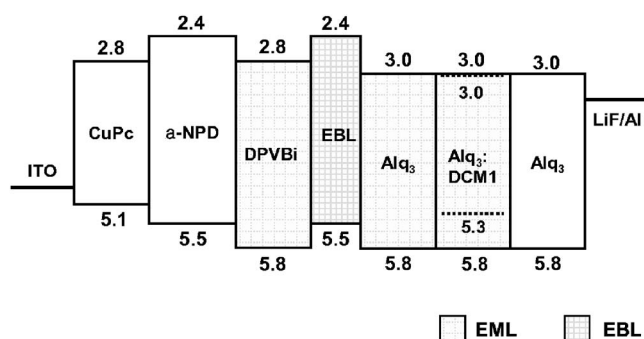

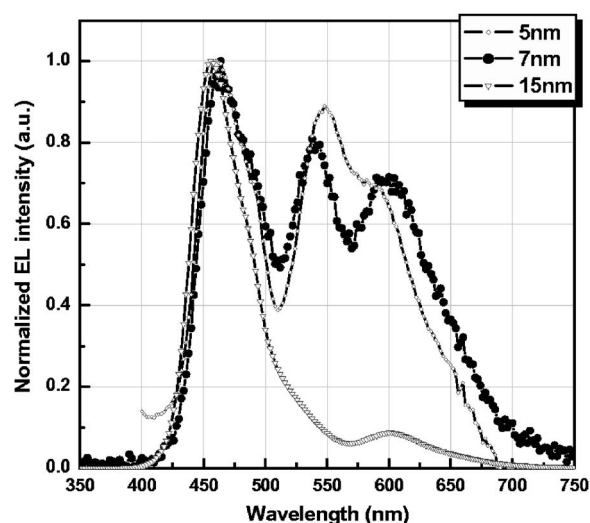**Figure 2.** The schematic energy band diagram of the investigated while OLEDs.

contribution from the red or a smaller contribution from the blue and green is needed to obtain the balanced white emission. Instead of increasing the red emission intensity, we reduced the contribution from blue emission. Thus, we proposed to control the contribution from blue emission by using the electron-blocking layer, which retards the flow of electrons into the blue-light-emitting layer, this way to reduce exiton formation in the blue-light-emitting layer. We fabricated devices with ITO/CuPc (3 nm)/α-NPD (40 nm)/blue (7 nm)/a-NPD (0.3, 0.5, and 1 nm)/green (7 nm)/red (7 nm)/Alq$_3$ (25 nm)/LiF:Al (150 nm) structure. We have selected α-NPD as the thin-EBL with some merits: (*i*) α-NPD has a wide energy bandgap, so it has a sufficiently high the lowest unoccupied molecular orbital (LUMO) level for pretty good electron blocking in the EML.[12] (*ii*) α-NPD was used as a prototypical HTL and generally acts also as an EBL with a simple process.[13,14] (*iii*) The glass transition temperature (T_g) of α-NPD is about 96°C; hence, it can enhance the stability of devices. To limit the electron transport into the blue-light-emitting layer, α-NPD is inserted between the blue-light-emitting layer and green-light-emitting layer. In this device, the LUMO of α-NPD is higher than that of the blue-light-emitting layer, so there is a large barrier (0.6 eV) for electron injection into the blue-emitting layer. Then we observed that the blue emission intensity weakened and that the emission of Alq$_3$ contributed to the broad tail at the long-wavelength region when α-NPD (1 nm) was inserted. This result showed that the exciton forms more in the red-emitting layer than the quantity of exciton created in the blue-emitting layer, that is, the α-NPD layer can effectively confine electrons in the green-emitting layer, so electrons could not easily be hopped into the blue-light-emitting layer, and the recombination rate decreased inside the blue-light-emitting layer.[15-18] The thickness of the blocking layer is an important parameter because it controls the spatial distribution of carriers.[19] In order to examine the dependence of the EL properties on the thickness of the thin-EBL, we fabricated devices with different α-NPD thicknesses. The EL spectra of (a) devices and (b) the CIE coordinates for different α-NPD thicknesses are shown in Fig. 4. Upon increasing the thickness of the α-NPD layer from 0.3 to 1 nm, emission from blue relatively decreases to that from red. This result showed that EL spectra depend on thickness of the α-NPD layer. When the thickness of the α-NPD layer is thick, the electrons are strongly blocked by α-NPD. Therefore, the most emission of the device is green, red. The CIE coordinates shift from red to white as decreasing thickness of α-NPD. It may result from the electron-trapping effect by α-NPD attributed to the increasing thickness, and the variation of the blue emission intensity could be un-
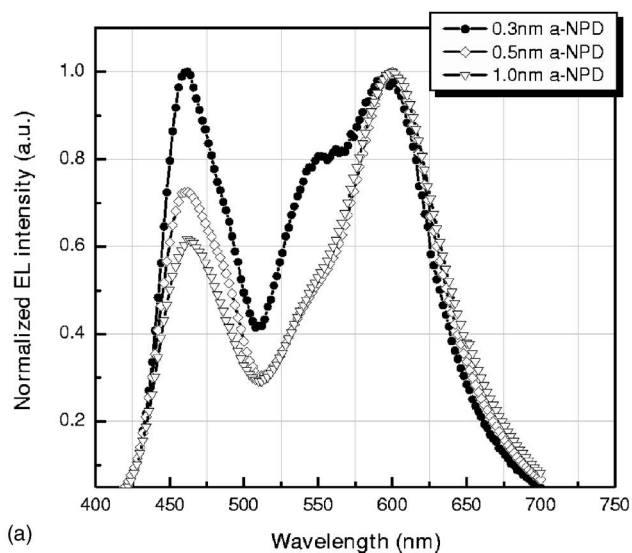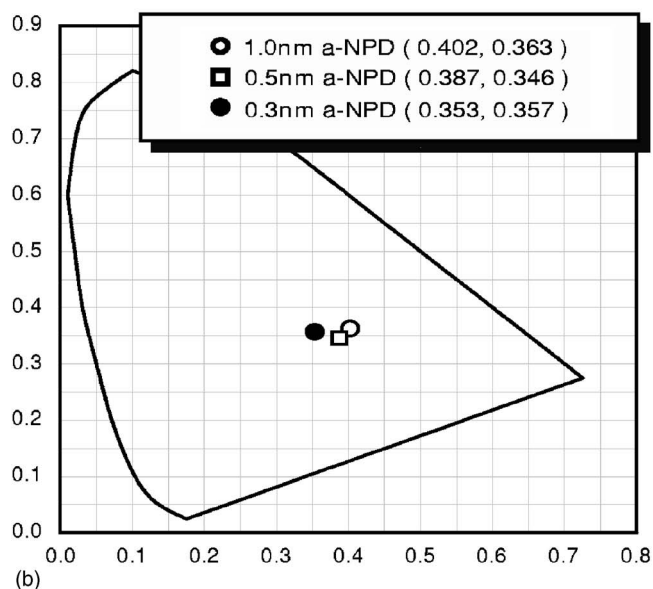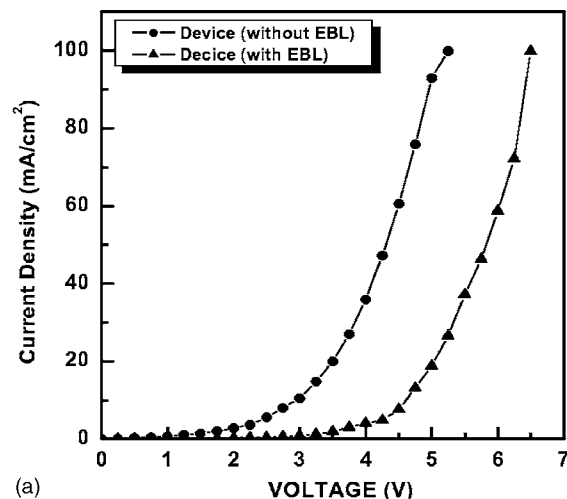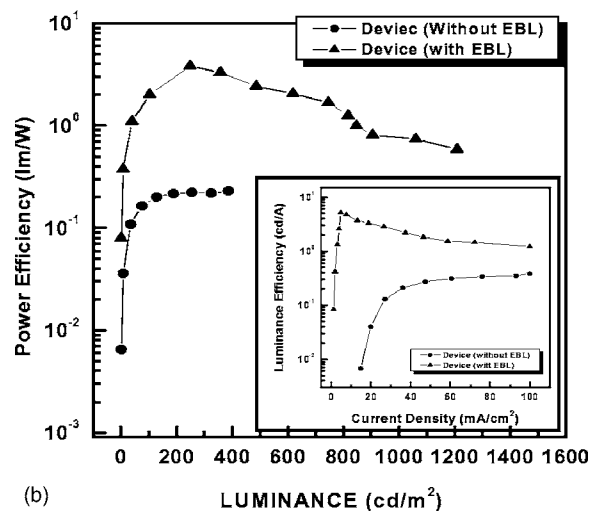
Figure 4. (a) The normalized EL spectra and (b) CIE chromaticity diagram under different thickness of thin-EBL (α-NPD).

Figure 5. (a) Current density vs applied voltage characteristics and (b) power efficiency vs luminance characteristics between the device with thin-EBL and without thin-EBL. (Inset) Luminance efficiency vs current density.

derstood as the result of α-NPD. That is, as the thickness of thin-EBL increases, it is more effective to block the electron and then the blue emission intensity decreases. The matching blue contribution relative to the red contribution can be achieved by controlling the thickness of α-NPD. From these results, we can consider that the balanced white emission was fabricated by using the thin-EBL (α-NPD) and controlling its thickness effectively.

Figure 5 shows J-V characteristics of devices (a) in which the thin-EBL was inserted with 0.3 nm thicknesses and was not. The insertion of the EBL increases turn-on voltage from 3 V for devices without α-NPD to 3.25 V for devices with an α-NPD layer. It indicated that the current density was influenced by the EBL, and the quantity of electrons tunneling through the barrier in the α-NPD/Alq$_3$ interface increases turn-on voltage. The efficiency is shown in Fig. 5b. The inset is the luminance efficiency vs current density. The device without the α-NPD had a maximum power efficiency of 0.2–0.22 lm/W at 142–255 cd/m^2 and a luminance of 300–400 cd/m^2 at 100 mA/cm^2, but in a device with 0.3 nm α-NPD, it had a maximum power efficiency of 3.80 lm/W at 250 cd/m^2, a luminance efficiency of 5.14 cd/A at 4.83 mA/m^2, and

a luminance of 1200 cd/m^2 at 100 mA/cm^2. These results indicate that the efficiency was also influenced by the thin-EBL. Moreover, this layer can also act as an exciton-blocking layer by preventing the exciton generated in the green, red emissive layer from hopping into the blue emissive layer.[20] This increases the exciton decay probability, causing increases in the efficiency of the device. This device closely matched the CIE coordinates (0.353, 0.357) of balanced white emission.

Conclusion

We have fabricated highly efficient white OLEDs by using α-NPD as thin-EBL. In a device with 0.3 nm thickness of α-NPD, the CIE coordinates were (0.353, 0.357) and well within the white region. Moreover, this device showed a maximum power efficiency of 3.80 lm/W at 250 cd/m^2, a luminance efficiency of 5.14 cd/A at 4.83 mA/m^2, and a luminance of 1200 cd/m^2 at 100 mA/cm^2, respectively. As the thickness of the EBL increases, the blocking of the electron happens effectively, hence the blue emission intensity decreases. Thus, we can consider that the optimum conditions of thin-EBL are effective in controlling emission intensity and balancing white emission. From the results, we can understand that thin-EBL played an important part in controlling the emission properties

of white OLEDs and improved efficiency. Thin-EBL will be a good means to obtain balanced emission and realize highly efficient white OLEDs.

References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2. J. Kido, M. Kimura, and K. Nagai, *Science*, **267**, 1332 (1995).
3. R. S. Deshpande, V. Bulović, and S. R. Forrest, *Appl. Phys. Lett.*, **75**, 888 (1999).
4. C. W. Ko and Y. T. Tao, *Appl. Phys. Lett.*, **79**, 4234 (2001).
5. B. W. D'Andrade, M. E. Thompson, and S. R. Forrest, *Adv. Mater. (Weinheim, Ger.)*, **14**, 147 (2002).
6. F. Steuber, J. Staudigel, M. Stössel, J. Simmerer, A. Winnacker, H. Spreitzer, F. Weissörtel, and J. Salbeck, *Adv. Mater. (Weinheim, Ger.)*, **12**, 130 (2000).
7. W. Xie, Z. Wu, and S. Liu, *Opt. Quantum Electron.*, **36**, 635 (2004).
8. C.-H. Kim and J. Shinar, *Appl. Phys. Lett.*, **80**, 2201 (2002).
9. M. Matsumura, K. Furukawa, and Y. Jinde, *Thin Solid Films*, **331**, 96 (1998).
10. H.-T. Lu and M. Yokoyama, *J. Cryst. Growth*, **260**, 186 (2004).
11. P. Jolinat, R. J. Clergereaux, J. Farence, P. Destruel, *J. Phys. D*, **31**, 1257 (1998).
12. R. Q. Zhang, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.*, **75**, 2418 (1999).
13. X. Y. Jiang, Z. L. Zhang, B. X. Zhang, W. Q. Zhu, and S. H. Xu, *Synth. Met.*, **129**, 9 (2002).
14. M. D. Halls, C. P. Tripp, and H. B. Schlegel, *Phys. Chem. Chem. Phys.*, **3**, 2131 (2001).
15. B. W. D'Andrade and S. R. Forrest, *Adv. Mater. (Weinheim, Ger.)*, **16**, 1585 (2004).
16. M. Ben Khalifa, D. Daufrey, and J. Tardy, *Org. Electron.*, **5**, 187 (2004).
17. Y. Xiaohui, H. Yulin, H. Yanbing, X. Zheng, and X. Xurong, *Displays*, **21**, 61 (2000).
18. S. T. Zhang, Z. J. Wang, J. M. Zhao, Y. Q. Zhan, Y. Wu, Y. C. Zhou, and X. M. Ding, *Appl. Phys. Lett.*, **84**, 2916 (2004).
19. S. S. Lee, T. J. Song, and S. M. Cho, *Mater. Sci. Eng., B*, **95**, 24 (2002).
20. S. Tokito, T. Iijima, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.*, **83**, 2459 (2003).