Color Stability of White Organic Light Emitting Diodes as Position of Partially Doped Rubrene in DPVBi Emission Layer

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Using blue emitting material, 4-bis(2,2-diphenylvinyl)-1,1-biphenyl (DPVBi) and orange dopant 5,6,11,12,-tetraphenyl-naphthacene (Rubrene), white organic light emitting devices (WOLEDs) have been fabricated. The location of rubrene doped definite thickness 50 A° in the emitting layer, DPVBi influences the electroluminescence (EL) and I-V characteristics are studied. As the gap from the NPD/DPVBi interface to the doped layer is increased, the intensity of blue peak enhances rapidly and turn-on voltage becomes higher. When doped layer is contacted with NPD, electroluminescence spectrum is seriously changed by applied voltage. However, devices with the gap, although this gap is very thin 0.5 nm, have good stability of color index by applied voltage.

Keywords: color index; doping; DPVBi; rubrene; spectrum; white organic light emitting diode (WOLED)

INTRODUCTION

White organic light emitting device (WOLED) has attracted considerable attention owing to various applications such as illumination light sources, light signs, and backlight in liquid-crystal displays (LCDs) [1,2]. Besides, a full color display has also been proposed using the WOLED and color filters [3]. This configuration has an advantage as

there is no need of fine shadow mask and to adopt the matured color filter process in LCD fabrication.

Many researchers have suggested various structures and materials to realize the WOLED [2–7]. White light is made up of nearly equal intensities of light in the visible region. However, WOLEDs are realized either by mixing three primary colors, red, green, and blue or complementary colors, blue and yellow. Particularly, it is important that emitting materials in two color system should have very broad emission spectra [7]. Since, it is difficult to obtain two or three color emissions from a single molecule with a balancing composition, more than one emitting organic specie are required which are arranged for efficient energy transfer.

In order to improve efficiency and color of WOLEDs, structures of devices have to be more complex, such as increasing number of layers and adopting multi emission layer. However, sufficient color stability is yet to realize in practical WOLEDs, especially the driving voltage induced color changes and the driving time are remained serious issues [6–7].

In the present investigation, we have fabricated WOLEDs using a very simple structure, having only the single emitting layer, DPVBi and the orange dopant, rubrene. DPVBi and rubrene used to realized WOLED emit complementary color, and their color index are (0.15, 0.16) and (0.46, 0.53), respectively. We designed the structure of WOLED with a definite doped layer to emit stable color as applied voltage. The fabricated white emitting devices are characterized by current-voltage-luminance (I-V-L) and electroluminescence (EL) measurements.

EXPERIMENTAL

Figure 1 shows the structure of fabricated devices used in this work. Commercially obtained ITO coated glass (Shinan SNP) anode with a sheet resistance of $9.8\,\Omega/sq.$ was patterned by photolithography and wet etching processes. The organic and metal cathode layers were deposited sequentially with shadow masks by thermal evaporation in a back ground pressure of 10^{-7} Torr and with a deposition rate of 1–$2\,\text{Å/s}$. The fabricated WOLED was composed of ITO, 4,4′,4″-tris [2-naphthyl(phenyl)amino] triphenylamine (2-TNATA), 4,4-bis[N-(1-naphtyl)-N-phenyl-amino] biphenyl(α-NPD), 4,4-bis(2,2-diphenylvinyl)-1,1-biphenyl (DPVBi):5,6,11,12,-tetraphenyl-naphthacene (Rubrene), tris-(8-hydroxyquinoline) aluminum (Alq3) and LiF-Al. The 400 Å thick layer of DPVBi was used as the blue emitting material and the host for the rubrene. The rubrene was partially doped in DPVBi layer.
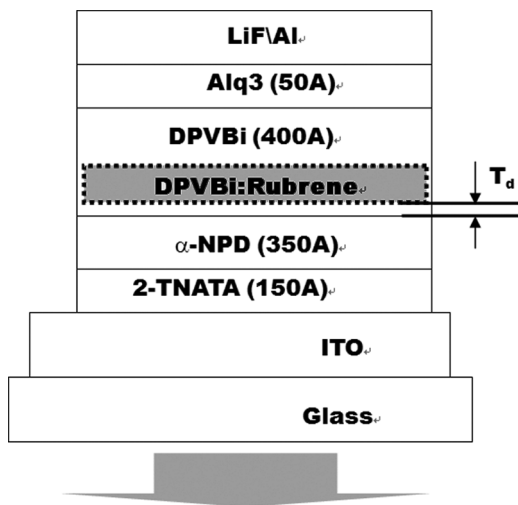
FIGURE 1 Structure of fabricated white OLED device. Here T_d is defined as the gap from the α-NPD/DPVBi interface to the rubrene doped in DPVBi layer.

Here, "T_d" is defined as the gap from the α-NPD/DPVBi interface to the rubrene doped in DPVBi layer. The position of rubrene doped layer in DPVBi controls the orange and sky blue emissions and hence the emission of final light from the device. The doping concentration was controlled from 0.06% to 0.18% but the width of the doped layer was fixed 5.0 nm thick.

Fabricated devices were encapsulated with a glass cap and UV sealant. All the devices have the emitting area of $0.4 \times 0.6 mm^2$. A Spectro-radiometer (Minolta CS1000) was employed for measurements of the electroluminescence (EL) spectrum. Current-Voltage (I-V) characteristics were measured with an experimental set-up consisting of a Keithley 2400 source meter and calibrated photodiode. Measurements and data acquisition were controlled by National Instrument's Lab VIEW software.

RESULTS AND DISCUSSION

To estimate the effect of the thickness of unoped layer between the α-NPD/DPVBi interface and the rubrene doped in DPVBi layer, we fabricated WOLEDs with different values of T_d. Figure 2 represents current density-voltage (I-V) curve of devices. Here, doping concentration and thickness of doped layer was fixed at 0.1% and 5 nm. As T_d was increased, turn-on voltage was shifted to high voltage.
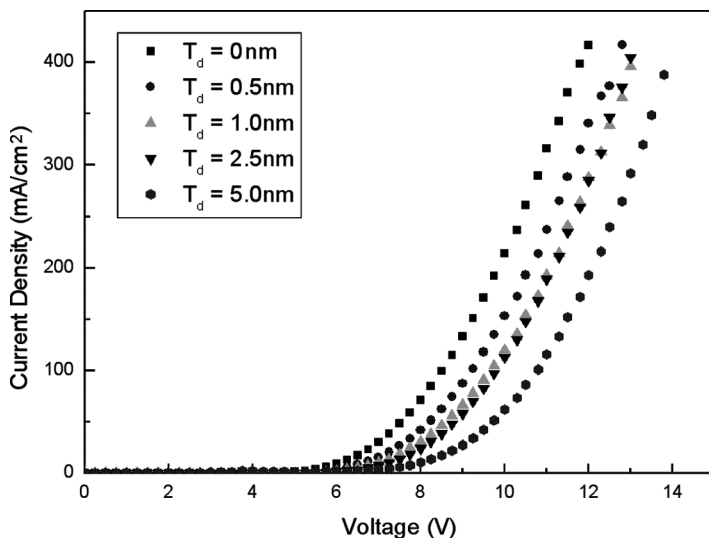
FIGURE 2 I-V characteristics curve as a function of T_d.

When doped layer was contacted with α-NPD layer, $T_d = 0$ nm, it had the highest current density at the same voltage. The rubrene molecules act as significant trap sites for most of the electrons injected from the LiF/Al cathode [8] at the doped region before reaching the α-NPD/DPVBi interface. And holes are accumulated at the α-NPD/DPVBi interface. So, high energy was required to diffuse holes into the doped region and recombined with trapped electrons in the doped region, resulting in alteration in I-V characteristic curves. Although, the total mass of the dopant material was same, electron transporting was obstructed as the rubrene doped layer was close to the cathode. As the number of electrons arrived at the α-NPD/DPVBi interface was decreased, recombination probability was diminished resulting in a high turn-on voltage.

Figure 3 shows normalized EL spectra of these devices. A blue peak at $\sim$445 nm was used as a normalization standard. The EL results in all devices showed two dominant peaks at 445 and 550 nm. In devices with $T_d = 0$ nm, the intensity of 550 nm peak (orange color) was stronger than that of the 445 nm peak. At $T_d = 0$ nm, the blue peak had a full width at half maximum (FWHM) of 65 nm while the orange peak at 550 nm along with a shoulder showed the FWHM of 88 nm. The shoulder peak at 575 nm was in the red region.

The intensity of orange peak was much sensitively changed by the thickness of T_d. With the value of $T_d = 0.5$ nm, the intensities of the
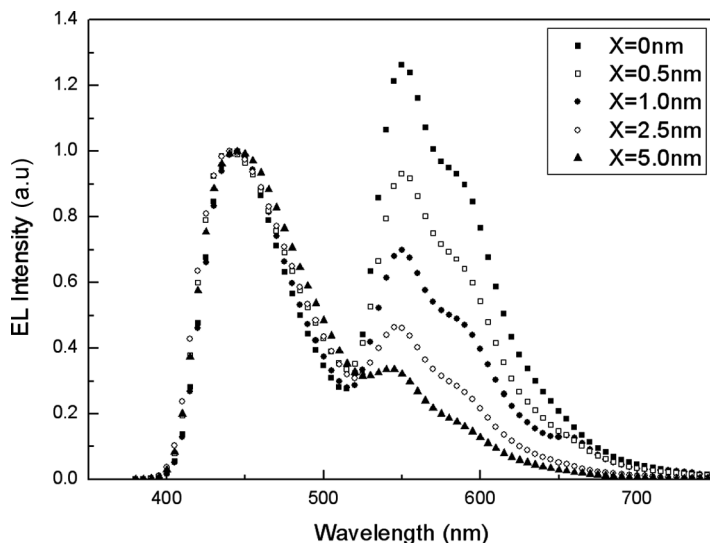
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FIGURE 3 EL spectra of fabricated devices as a function of T_d at 9 V.

two main peak became analogous. In contrast to device with $T_d = 0$ nm, the intensity of the shoulder in the red region in a device with $T_d = 5$ nm became weaker and the peak was narrow (FWHM = 73 nm). When T_d was over 2.5 nm, the EL spectrum was composed of the strong blue peak and the weak and broad orange peak.

Color stability in WOLED is an important issue in manufacturing. WOLEDs accompanying with stable color as a function of applied voltages is meaningful practical applications. Figure 4 shows CIE color indexes as a function of applied voltage and T_d. The device $T_d = 0$ nm showed serious shift by applied voltage from (0.387, 0.464) at 6 V to (0.285, 0.316) at 9 V. In the WOLED used DPVBi and rubrene, the excitation of DPVBi emitted blue light and partially transferred its energy to rubrene molecules, so white was realized by the balance of two complementary colors. When $T_d = 0$ nm, excited energy in DPVBi mainly transferred to rubrene. Furthermore, the rubrene molecules formed excitons directly [9]. At the low voltage, most exciton was formed the near α-NPD/DPVBi interface, so orange light by rubrene was dominant but blue light by DPVBi is weak. However, as applied voltage was increased, the emission from DPVBi was larger than rubrene. In this system, rubrene molecules were not sufficient in number to receive the whole excited energy from DPVBi molecules to emit orange light. Therefore, as the applied voltage was increased,
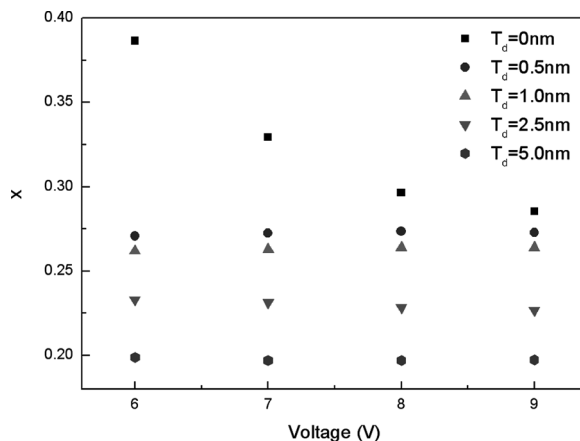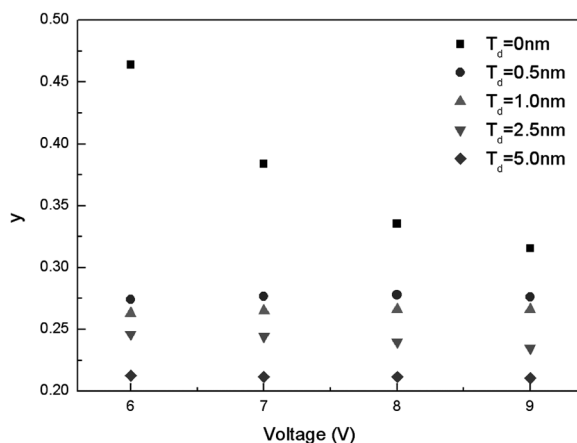
FIGURE 4 Color coordination of fabricated WOLEDs with different T_d from 0 nm to 5.0 nm.

the blue emission owing to the excited energy by DPVBi was more augmentative than orange emission. As a consequence, the CIE color index was significantly shifted from orange to blue with the applied voltage.

Contrary to device with $T_d = 0$ nm, devices with gap, although thickness of gaps was different, showed the small deviation of color index by applied voltage. At the device with $T_d = 0.5$ nm, CIE color index showed the little change from (0.271, 0.274) at 6 V to (0.273, 0.276) at 9 V. The DPVBi emission peaks at $\sim$460 nm while the rubrene
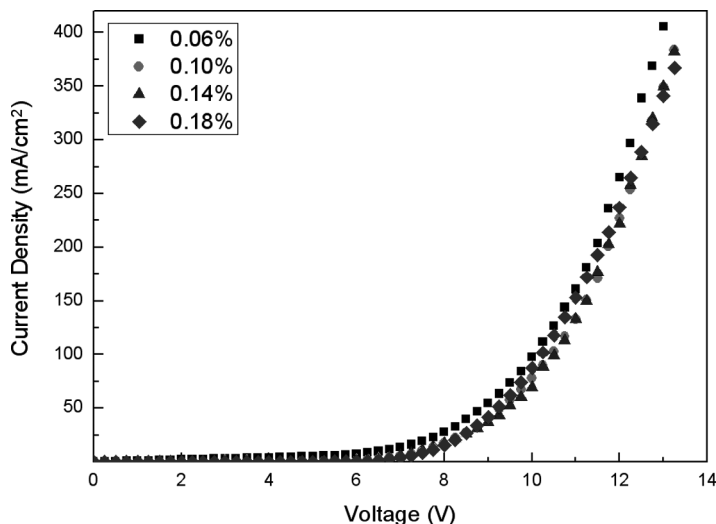
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FIGURE 5 I-V characteristics curves of WOLEDs as a function of doping concentration $0.06\% \sim 0.18\%$. The T_d and the thickness of doped layer is fixed as 0.5 nm and 5 nm, respectively.

absorption peaks appeared at 460 nm, 490 nm and 529 nm. Therefore, the efficient energy transfer from DPVBi to rubrene molecules was due to the Förster energy transfer mechanism [6,10–11]. Föster energy transfer is operative for host-guest separation of up to $40 \sim 100$ Å. So, even in a device with $T_d = 5$ nm, doped rubrene molecules in the definite doped layer (5 nm) could be able to contribute the emission of orange light. It seems that the energy transfer from the DPVBi to rubrene maintained the steady ratio irrespective of the value applied voltage. Also this ratio of energy transfer was decreased as T_d became thicker.

Devices were fabricated as different doping concentration when T_d and thickness of doped layer is fixed as 0.5 nm and 5 nm, respectively. Figure 5 shows I-V characteristic curve of fabricated devices. Although device with 0.06% doping concentration had the lowest turn-on voltage, four devices represented similar I-V characteristic curve. As compared with Figure 2 as a function of T_d, I-V was dominated by the location of doped layer in the emitting layer than the mass of dopant.

As doping concentration was increased, the color index was allowedly shifted as the line from blue of DPVBi (0.15, 0.16) toward orange (0.46, 0.53) of rubrene (Fig. 6). Without regard to doping concentration, devices with gap maintained the excellent color stability without
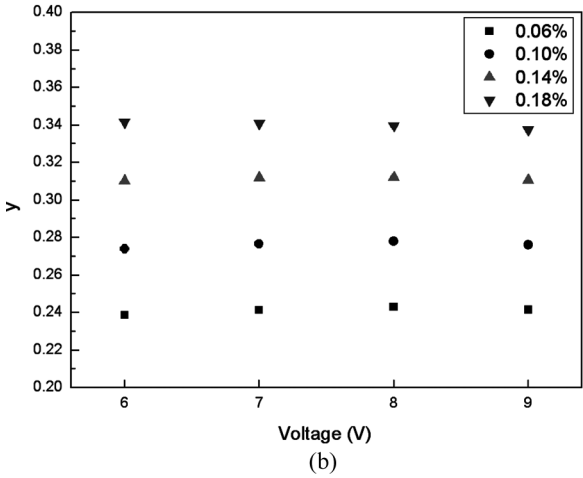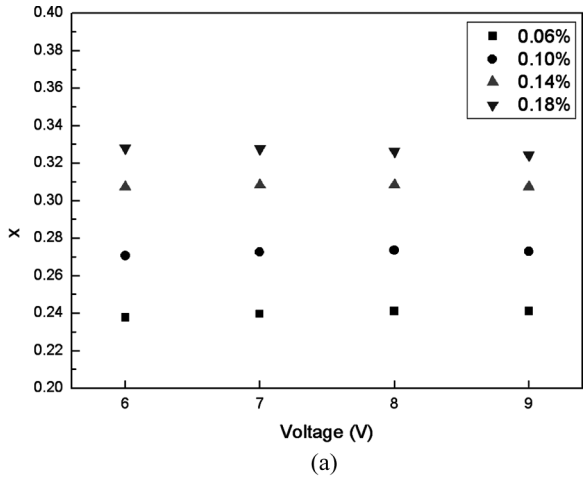
FIGURE 6 Color coordination of WOLEDs by doping concentration 0.06% ∼ 0.18%.

regard to the applied voltage. The device with 0.18% showed the good white, (0.328, 0.342) at 6 V and (0.324, 0.338) at 9 V. At 9 V, brightness and efficiency of device was 2,225 cd/m^2 and 5.85 cd/A.

CONCLUSIONS

We had fabricated WOLEDs using mixing of two colors, blue and orange. WOLEDs are realized by i) doping the rubrene in DPVBi

ii) confining the definite thickness of doped layer to 50 Å, and iii) varying the gap from NPD/DPVBI interface to doped layer, $T_d = 0–5$ nm. The degree of energy transfer from DPVBi to rubrene is controlled by T_d. When T_d is zero, color index is seriously shifted by applied voltage, so it is not suitable to realize a stable WOLED. As device has a thin gap, T_d, its color is maintained without regard to applied voltage. I-V characteristics curves of devices are affected by T_d than doping concentration. Device with $T_d = 0.5$ nm and 0.18% doping concentration has a good color index (0.324, 0.338) at 9 V and nearly constant without regard to applied voltage.

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