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Color-tunable white organic light-emitting diodes with a micro-cavity and an external phosphor conversion layer

Shui-Hsiang Su*, Wen-Yu Wang, and Yen-Sheng Lin
Department of Electronic Engineering, I-Shou University, Kaohsiung City, Taiwan 840, R.O.C.
**Corresponding Author: Shui-Hsiang Su*

ABSTRACT: White organic light-emitting diodes (WOLEDs) have been fabricated by combining a blue phosphorescent OLED with an external phosphor conversion layer (PCL). The PCL is formed from red $CaMoO_4:Eu^{3+}$ phosphor by spin-coating technique. By adjusting the thickness and concentration of PCL, a white light emission with the CIE coordinates of (0.32, 0.40) is obtained. At the same time, the WOLED shows an optimal luminous efficiency of 27.5 cd/A. The CIE surrounds pure white light (0.33, 0.33) and can be tunable in a wide range by varying PCL coating speed. Moreover, utilizing a micro-cavity in the blue OLED structure to fabricate WOLED with a coated-PCL, the WOLED demonstrates the CIE coordinate of (0.30, 0.34), which is close to the position of pure white light (0.33, 0.33).
Key words: white organic light-emitting diodes, phosphor conversion layer

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted much interest over the past few years because of their properties of self-emission, fast response time, high luminance, low cost, and ease of fabrication [1-2]. In particular, white OLEDs (WOLEDs) have drawn particular attention because of their use in full-color displays combined with red-green-blue (RGB) color filters, liquid crystal display (LCD) backlights, and next-generation light sources [3-6]. White light emission can be obtained by mixing light of two complementary colors (such as red/bluish green, blue/orange, or green/magenta) or the three primary colors (red, green, and blue) from small molecules and/or polymers. To obtain high luminance of a typical layered OLED, the light-emitting layer is generally doped with various fluorescent or phosphorescent dyes [7-10]. Such doping is performed using a multilayer structure with two or more emitting layers. However, single emissive layer of the WOLEDs have to be carefully adjust the doped light emitting materials concentrations to avoid color diversity. Multiple emissive layers exhibit color shift with driving current change or operating times due to the differential aging of different emitting materials. In a tandem OLED structure, in which individual electroluminescent (EL) elements are electrically connected in series, luminous efficiency scales almost linearly with the number of EL units in the tandem [11-14]. The interconnecting layer, which connects adjacent emissive units, markedly affects device performance and hard to be found candidate materials. Moreover, a WOLED combining the blue OLED with inorganic phosphor conversion layer (PCL) had been first successfully fabricated, but showed a low luminous efficiency of 3.76 lm/W [15]. It showed a stable and easier fabrication process. Lots of published studies, including using sandwiched color conversion layer (CCL) [16], hybrid CCL [17], and transparent OLED with a CCL [18], had intended to enhance the luminous efficiency but poor results or even resulting in a complicated device structure.

In this work, PCL has been formed of a spin-coated inorganic red phosphor onto glass substrate and combining a blue fluorescent OLED to fabricate the WOLED. Furthermore, a micro-cavity blue OLED is proposed to study the CIE coordinates of WOLED. The optoelectronic characteristics of WOLEDs are analyzed and discussed.

II. EXPERIMENT

Figure 1(a) schematically depicts the WOLED architectures with a PCL, in which white emission was obtained by mixing emission of complementary blue and red color. Fig. 1(b) shows the micro-cavity blue OLED, which is constructured by inserting a silver (Ag) metal thin film between ITO anode and a hole injection layer (HIL) to act as a semi-transparent reflection anode. The glass substrates had been pre-coated with a 200-nm-thick layer of indium-tin-oxide (ITO) with a sheet resistance of 7 □/square. The PCL was first spin-coated on the glass face of ITO/glass substrate before the blue OLED fabrication.

A binder mixed with red phosphor $CaMoO_4:Eu^{3+}$ at various proportion. The phosphor mixture was stirred using an axis drum mixer for 15 min to produce uniform slurry, which was vacuumed for 20min in a vacuum chamber to remove the air bubbles. The phosphor slurry was spin-coated on the glass side of the substrate with various coating speeds, which could vary and form PCL film in different thicknesses. The PCL was subsequently dried at 150ºC for 30 min.

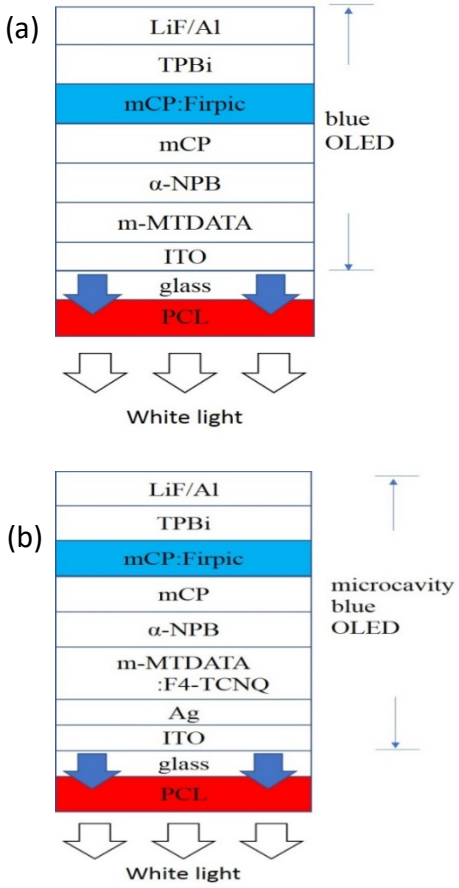

Figure 1: The WOLED architectures with (a) a blue OLED and PCL, (b) a micro-cavity blue OLED and PCL.

After the drying process, the PCL-coated ITO/glass substrate was loaded into an evaporation equipment at a base pressure of under 10^{-6}Torr for fabricating the blue OLED on the face of ITO. The structure of blue OLED used in this study is ITO/m-MTDATA(105 nm)/α-NPB(20 nm)/mCP(10 nm)/mCP:FIrpic(30 nm, 10%)/TPBi(40 nm)/LiF/Al. Herein, m-MTDATA, α-NPB, TPBi and LiF act as the hole injection layer (HIL), hole transporting layer (HTL), electron transporting layer (ETL), and electron injection layer (EIL), respectively. mCP doped with 10% FIrpic is the emitting layer (EML). All the organic layers were sequentially deposited at a rate 1~2 A/s onto PCL-coated ITO/glass substrates by thermal evaporation from resistively heated tantalum boats, at a base pressure below 10^{-6} Torr. The evaporation rate and thickness of the film was determined using an oscillating quartz thickness monitor (Sycon STM-100). Finally, a 200-nm-thick layer of Al was thermally evaporated as a cathode without breaking the vacuum. All devices were encapsulated in a dry nitrogen glove box that contained O and H_2O at concentrations of under 1 ppm. The blue OLEDs were formed such that the intersections between the ITO anode and the cathode stripes each had an area of 0.24 cm^2.

The luminance-current density-luminous efficiency characteristics were measured using a PR650 spectroscan spectrometer and a Keithley2400 programmable voltage-current source. The EL spectra and the Commission Internationale d'Eclairage (CIE) coordinates of these devices were also obtained using a PR650 spectroscan spectrometer. These instruments were connected to a personal computer and controlled using Labview software. All of the measurements were conducted in air at room temperature.

III. RESULTS AND DISCUSSION

To excite the phosphor in the PCL effectively, it deserves a stable and high luminous efficiency blue OLED as the excitation light source. By adding an additional mCP layer next to the EML to adjust the p-terminal thickness, we discuss the limitation effect of the triplet exciton in the EML. As shown in Fig. 2, it can be observed that after inserting 10 nm mCP, the overall luminous efficiency is enhanced, from 16.8 cd/A to 20.8 cd/A. Before the mCP was inserted, large energy barrier exists at the α-NPB/EML interface, which results in lots of holes directly jump to FIrpic HOMO and only a few holes jump to the mCP HOMO in EML. The probability of the electron-hole recombination in mCP EML is decreased, which will reduce luminous efficiency. After inserting mCP, therefore, more holes coming from α-NPB will move into the mCP blocking layer, and then transfer to the mCP HOMO in EML to recombine with electrons.

Another phenomenon is that the materials used for EML are phosphorescent materials and the triplet excitons have a longer lifetime. The diffusion distance will become longer and it is easier to diffuse. As illustrated in Fig. 3, the mCP triplet energy is 2.9 eV higher than FIrpic of 2.65 eV. mCP with high triplet energy is inserted between α-NPB and EML to be the triplet exciton blocking layer. At the same time, the TPBi ETL also has a triplet energy of 2.8 eV and almost all triplet excitons in the EML are confined, so that the efficiency can be improved. Therefore, the optimal blue OLED structure is ITO/m-MTDATA (30 nm)/α-NPB (20 nm)/mCP (10 nm)/mCP:FIrpic (30 nm, 10%)/TPBi (40 nm)/LiF/Al. The EL spectrum shown in Fig. 4 exhibit an emission at 472 nm and the shoulder peak at 500 nm. When the blue OLED is driven from 5 to 160 mA/cm^2, the EL spectra hardly change. The blue OLED is suitable to be used as a

stable excitation light source for PCL.

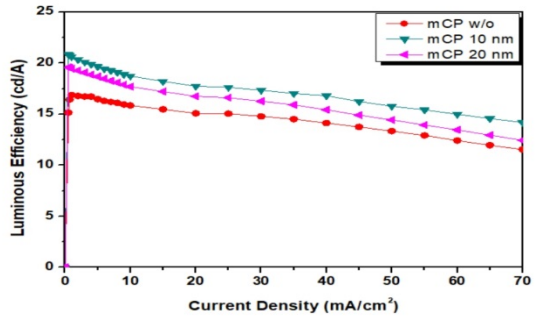

Figure 2: Luminous efficiency-current density characteristics of blue OLED.

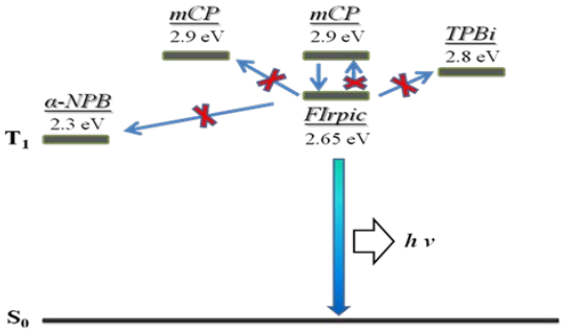

Figure 3: Triplet energy level diagram of blue OLED.

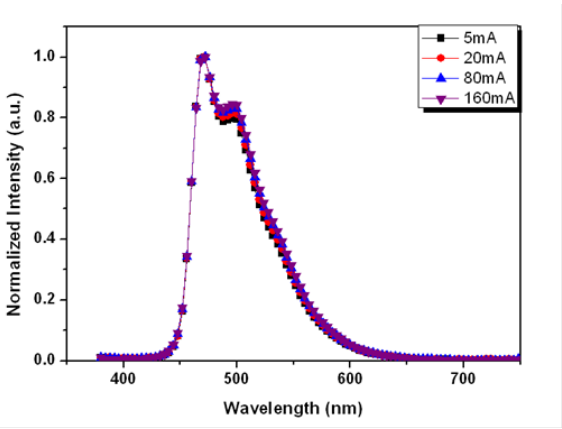

Figure 4: The EL spectra of blue OLED driven from 5 to 160 mA/cm^2.

The photo luminescence (PL) spectra of the $CaMoO_4:Eu^{3+}$ PCL was excited by 470 nm and detected. 470 nm corresponds to the main emission light of blue OLED as indicated in Fig. 4. The PCL shows emission band ranging from 500 to 700 nm. It reveals that the process of the energy transfer from the blue OLED to PCL indeed happens in the WOLED device. During experiment, the coating speed is varied from 1000 to 2500 rpm to modulate PCL thickness. When the coating speed becomes slower, the PCL thickness is thicker and PL intensity of the PCL becomes stronger. Therefore, in addition to the blue OLED, the thickness of the PCL is also one of the factors affecting the characteristics of white OLED. The intensity of EL spectra of WOLED under the current density of 20mA/cm^{2}are illustrated in Fig. 5 (a). The coating speeds of PCL varies from 1000 to 2500 rpm by fixing the concentration ratio of the phosphor powder slurry at 20 wt.%. The PCL formed at a coating speed of 2500 rpm becomes thinner and most of the blue light does not participate in the photon excitation reaction. Blue light directly penetrates the PCL and the excited phosphor will also be relatively reduced. This phenomenon can be found at the position between 600 ~ 700 nm. The EL intensity of PCL in red emission decays with the coating speed increasing from 1500 to 2500 rpm. Fig.5(b) shows the CIE (x, y) coordinates of WOLED driven at a current density of 20mA/cm^2. It can be found the CIE coordinates of WOLEDs with a PCL at coating speed of 1000 ~ 2500 rpm distributed in the white light region. The CIE coordinates are (0.40, 040), (0.32, 0.40), (0.28, 0.40) and (0.24, 0.38) when a PCL at coating speed of 1000, 1500, 2000 and 2500 rpm, respectively.

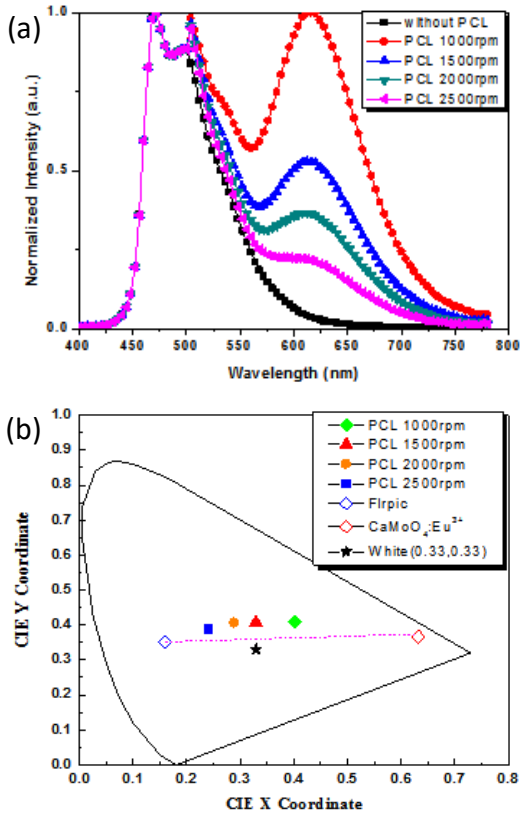

Figure 5: (a)The EL spectra of WOLED driven at 20mA/cm^2, (b)CIE coordinates of WOLED driven at a current density of 20mA/cm^2.

The dependence of luminous efficiency of WOLEDs on current density is shown in Fig. 6. When varying coating speed from 1000 to 2500 rpm, the luminance efficiency increases firstly and then decreases. It can be found that the luminous efficiency

of the WOLED with a PCL at coating speed of 1500 rpm reaches an optimal of 27.5 cd/A. It indicates a PCL at the appropriate thickness let the fabrication of high efficiency WOLED be realized. For further improve the CIE coordinates of WOLED close to pure white light (0.33, 0.33), a micro-cavity blue OLED is proposed shown in Fig. 1 (b). The length of the resonant cavity is adjusted by modulating the thickness of the HIL (m-MTDATA:F4-TCNQ). Comparing to the blue OLED shown in Fig. 1(a), the EL spectra of micro-cavity blue OLED are much narrower and shows a deep blue emission. Fig. 7 shows the CIE coordinates of WOLED driven at a current density of 20mA/cm^2. A WOLED consisting of a micro-cavity blue OLED coated with a PCL demonstrates the CIE coordinates (x, y) of (0.30, 0.34), which is close to the position of pure white light (0.33, 0.33).

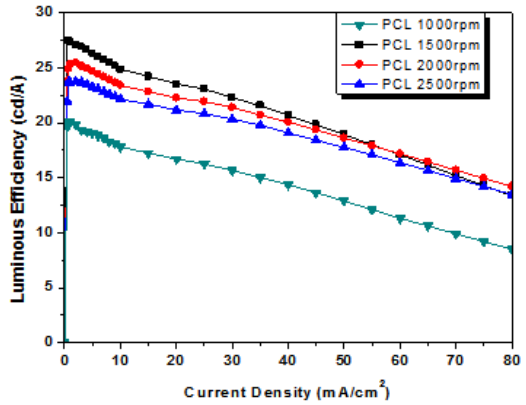

Figure 6: The dependence of luminous efficiency of WOLEDs on current density.

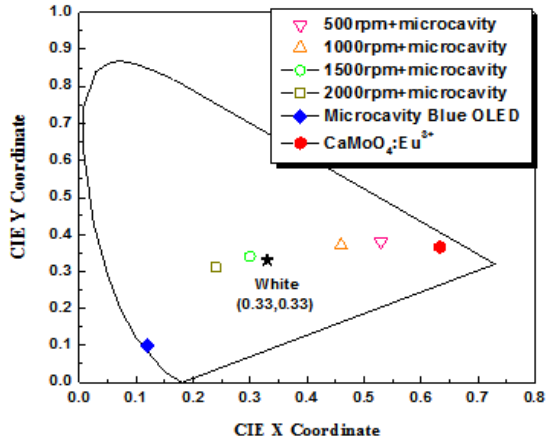

Figure 7: The CIEcoordinates of WOLED driven at a current density of 20mA/cm^2. A micro-cavity blue OLED is also indicated.

IV. CONCLUSION

WOLEDs have been successfully fabricated by combining a blue OLED with a red PCL. Experimental results reveal that the red light can be emitted from a PCL owing to be excited by the light from a blue OLED and then mixes the unabsorbed blue emission to produce white light emission. The PCL is formed from red $CaMoO_4:Eu^{3+}$ phosphor by spin-coating technique. When the concentration ratio of the phosphor powder slurry is 20 wt.% and the coating speed is 1500 rpm, the WOLED exhibits a white light emission with the CIE coordinates of (0.32, 0.40). At the same time, the WOLED shows an optimal luminous efficiency of 27.5 cd/A. The CIE surrounds pure white light (0.33, 0.33) and can be tunable in a wide range by varying PCL coating speed. Moreover, utilizing a micro-cavity in the blue OLED structure to fabricate WOLED with a coated-PCL, the WOLED demonstrates the CIE coordinate of (0.30, 0.34), which is close to the position of pure white light (0.33, 0.33).

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