

Low-Molecular-Weight White Organic-Light-Emitting-Devices using Direct Color Mixing Method

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Abstract

In order to achieve white emission from organic light emitting devices (OLEDs), five distinct structures were fabricated and tested. The white emission was obtained using two different color-emitting materials (yellow from rubrene-doped Alq₃ and blue from DPVBi) with or without a carrier-blocking layer. For enhancing the red emission, two types of devices with three-color emitting materials were fabricated. The white emission, close to the CIE coordinate of (0.3,0.3), was achieved by using two blocking layers as well that as without a blocking layer. This paper covers the subject of controlling the location of exciton recombination zone. It has been found that there is a trade-off in that the devices with three color emitting layers do not show as much luminescence efficiency compared to those with two color emitting layers, but rather, show distinct red emission in the resultant emission spectra. The highest power efficiency was measured to be 1.15 lm/W at 2,000 cd/m² for a structure with two color-emitting layers.

Keywords : white light emitting device; carrier blocking; exciton recombination

1. Introduction

Characteristics such as wide viewing angle, fast response, low power consumption, and the possibility of wide application has spurred interest in organic light emitting diodes (OLEDs) [1-3]. Since its first report by Tang and Vanslyke in 1987 [4], it organic light emitting has become an active field of research [5-7]. Several studies have been reported on white organic electro luminescent (EL) devices [1-8].

Two methods to modify the spectral characteristics of an OLED to achieve white emission have been demonstrated [9-11]. First, doping the emission layer

with a luminescent dye as a dopant can cause energy to be transferred from the host to the dopant or carrier trapping at the dopant site. Such energy transfer is always incomplete which in turn can result in light being emitted from both the host and the dopant. This technique has been used for obtaining white light emission from small-molecule-based multi-layer devices comprising two or three different layers, each emitting one color or a combination of three primary colors. Second, sandwiching a layer that preferentially blocks one type of carrier between the hole-transporting layers (HTL) and electron-transporting layers (ETL) can control the spatial location of the exciton recombination zone in order to achieve white emission via direct color mixing [12]. It has been demonstrated that different colors can be mixed to generate white emission by controlling the thickness of the blocking layers. This is because it allows the spatial distribution of carriers across the blocking layers to be changed. Using three different color-emitting layers for the white emission is somewhat straightforward even though the structure is more complex. A pioneering work for obtaining the

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white emission has been first published by Kido *et al.* [7]. Recently, an improved method for the white-light emission was reported by Deshpande *et al.* [8]. They concluded that energy transfer occurs in a sequential manner between species in different layers across the thin hole blocking layer, so called, the interlayer sequential energy transfer. In the studies when three different color emitting layers, were used the emitting color was tuned to white by controlling both the thickness of the blocking layer and the concentration of dopant. Therefore, the structure should be considered to not only use the carrier-blocking layer, but also the incompleteness of energy transfer between the host and dopant. But, using the blocking layer has a drawback of blocking the movement of carrier resulting in the reduction of the power efficiency of the device.

In this paper, three types of multi-layer white light-emitting devices were fabricated and tested, which are two-color and three-color devices with blocking layers, and devices without a blocking layer. The first two types use blocking layers to control a spatial distribution of carriers across the blocking layers and the third controls the spatial distribution of excitons by controlling the thickness of emission layer instead of using a blocking layer.

2. Experiment

A glass substrate pre-coated with an ITO thin film with a sheet resistance of $10 \Omega/\square$ was cleaned by wet cleaning method and photo-lithographically patterned to form the transparent anode. The wet cleaning method included sonification by de-ionized (DI) water, degreasing by flushing in warm TCE, rinsing in acetone and methanol, and finally rinsing in DI water. On top of the anode a buffer layer of phthalocyanine copper complex (CuPc) was deposited by vacuum sublimation in order to enhance the hole injection from the anode. We used 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD) as the HTL and α -NPD was used as an electron-blocking layer between two emissive layers. We used 4,4'-bis(2,2-diphenyl-ethen-1-yl)-diphenyl (DPVBi) as a blue emitting material, 5,6,11,12-tetraphenyl-naphthacene (Rubrene) as a yellow emitting dopant, 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) as a red dopant and tris-(8-hydroxy-chinolinato)-aluminum

(Alq₃) as a yellow and red host.

We select two combinations of emission-color. First DPVBi and rubrene-doped Alq₃ was selected. Second, a combination of DPVBi, Alq₃ and DCJTB-doped Alq₃ was selected as emissive materials. The reason for selecting these combinations is that direct mixing of the two colors emitted from those materials could produce white emission at a certain balance. Depending on the thickness of the carrier-blocking layer, the thickness of the each emission layer and the applied voltage, the spatial location of exciton recombination zone could change, and the color emitted from the OLEDs is subject to change. Alq₃ was used on top of the emissive layers as an ETL. All the organic layers were thermally deposited at an approximate growth rate of 1-2Å/s. For a cathode electrical contact, Al:Li alloy was finally capped over the organic layers which were thermally sublimated in vacuum of less than 10^{-6} torr. Current-voltage characteristics and luminescence intensity were measured using a Kethley 236 measure unit and a silicon photodiode calibrated with a luminance meter (Minolta CS-100). And electroluminescent spectra were measured with a fiber optic spectrometer (S2000). Current-voltage characteristics, luminance intensity and spectra were measured at the same time.

3. Results and Discussion

The organic light-emitting-device (OLED) structures studied in this work are schematically shown in Fig. 1. As shown in Fig. 1, five different OLED structures were fabricated and tested. Figs. 1 (a), (b) and (c) are white OLEDs that use two different color-emitting layers and Figs. 1(d) and (e) are OLED structures that use three different color-emitting layer. Devices with structures (a), (b) and (d) were fabricated with blocking layers to control the movements of carriers. Structure (e) was composed of three different color-emitting layers, while the blocking layers were omitted. With this structure, the effect of blocking layer and the location where the exciton recombination took place can be understood.

In the device structures that have the blocking layer, white color-emission could be achieved by adjusting the thickness of blocking layers. For the OLED structure(a)

	thickness
Cathode(Al:Li)	100nm
ETL(Alq_3)	50nm
Yellow(Alq_3 : Rubrene , 5wt%)	15nm
blocking layer(α - NPD)	2 - 4nm
Blue(DPVBi)	15nm
HTL(α - NPD)	50nm
CuPc	15nm
Anode(ITO substrate)	

(a)

	thickness
Cathode(Al:Li)	100nm
ETL(Alq_3)	50nm
Blue(DPVBi)	15nm
blocking layer(α - NPD)	1 - 7nm
Yellow(Alq_3 : Rubrene , 5wt%)	15nm
HTL(α - NPD)	50nm
CuPc	15nm
Anode(ITO substrate)	

(b)

	thickness
Cathode(Al:Li)	100nm
ETL(Alq_3)	50nm
Yellow(Alq_3 : Rubrene , 5wt%)	20nm
Blue(DPVBi)	5nm
HTL(α - NPD)	50nm
CuPc	15nm
Anode(ITO substrate)	

(c)

	thickness
Cathode(Al:Li)	100nm
ETL(Alq_3)	50nm
Blue(DPVBi)	15nm
blocking layer(α - NPD)	5nm
Green(Alq_3)	15nm
blocking layer(α - NPD)	2, 5.3nm
Red(Alq_3 : DCJTb , 5wt%)	15nm
HTL(α - NPD)	50nm
CuPc	15nm
Anode(ITO substrate)	

(d)

	thickness
Cathode(Al:Li)	100nm
ETL(Alq_3)	50nm
Red(Alq_3 : DCJTb , 5wt%)	15nm
Green(Alq_3)	15nm
Blue(DPVBi)	15nm
HTL(α - NPD)	50nm
CuPc	15nm
Anode(ITO substrate)	

(e)

Fig. 1. The schematic cross section of fabricated OLED structure.

In Fig. 1, two different colors of yellow (Rubrene-doped Alq_3) and blue (DPVBi) were deposited with a blocking layer (α -NPD) in between the two layers. Since the yellow color is composed of red and green colors, it is expected that the white emission could be achieved by adjusting the mixing amount of the yellow and blue colors. Adjusting the thickness of blocking layer in between the two layers could control the degree of color mixing. As shown in Fig. 2 (a), the resulting electroluminescent color is composed of two colors of yellow and blue, as expected, for both cases of the blocking layer thickness of 2 and 4 nm. In the case of thicker blocking layer used, the yellow emission was found to be stronger since electrons were blocked more severely by the thick blocking layer. If there was no blocking layer used, the color emission should have been near the pure blue from DPVBi due to nonblocking of electrons. So, the role of blocking layer could be answered as predominant blocking of electrons prior to exciton recombination. As shown in Fig. 3 (a), α -NPD has a higher LUMO level compared to that of Rubrene-doped Alq_3 and higher HOMO level than that of DPVBi, so that electrical carriers are blocked at the interfaces and the recombination depends on the degree of tunneling of carriers through the blocking layer. In case where non blocking layer are used, the recombination is expected to occur predominantly in the region of blue emission due to larger discontinuity in LUMO level energy at the interface between the HTL and blue emission region. The blocking layer can be said to make a role for dividing the recombination zone, resulting in color mixing as the result.

In case of the OLED structure with 2nm-thick blocking layer, as shown in Fig. 1 (a), the emission color was observed to be near yellow at low operating voltaged. As the voltage increased, the emission color tend to shift toward the blue color, resulting in the white emission around 15 V. The change in the color coordinate is shown in Fig. 4 (a). The color emission from the structure with 4nm-thick blocking layer was found to start around white at low voltages and end up with blue at high voltages. Therefore, it could be concluded that the emission color is very sensitive to the operating voltage in this structure. When the position of two different emitting layers was interchanged as shown in Fig. 1 (b), the resulting color emission could be

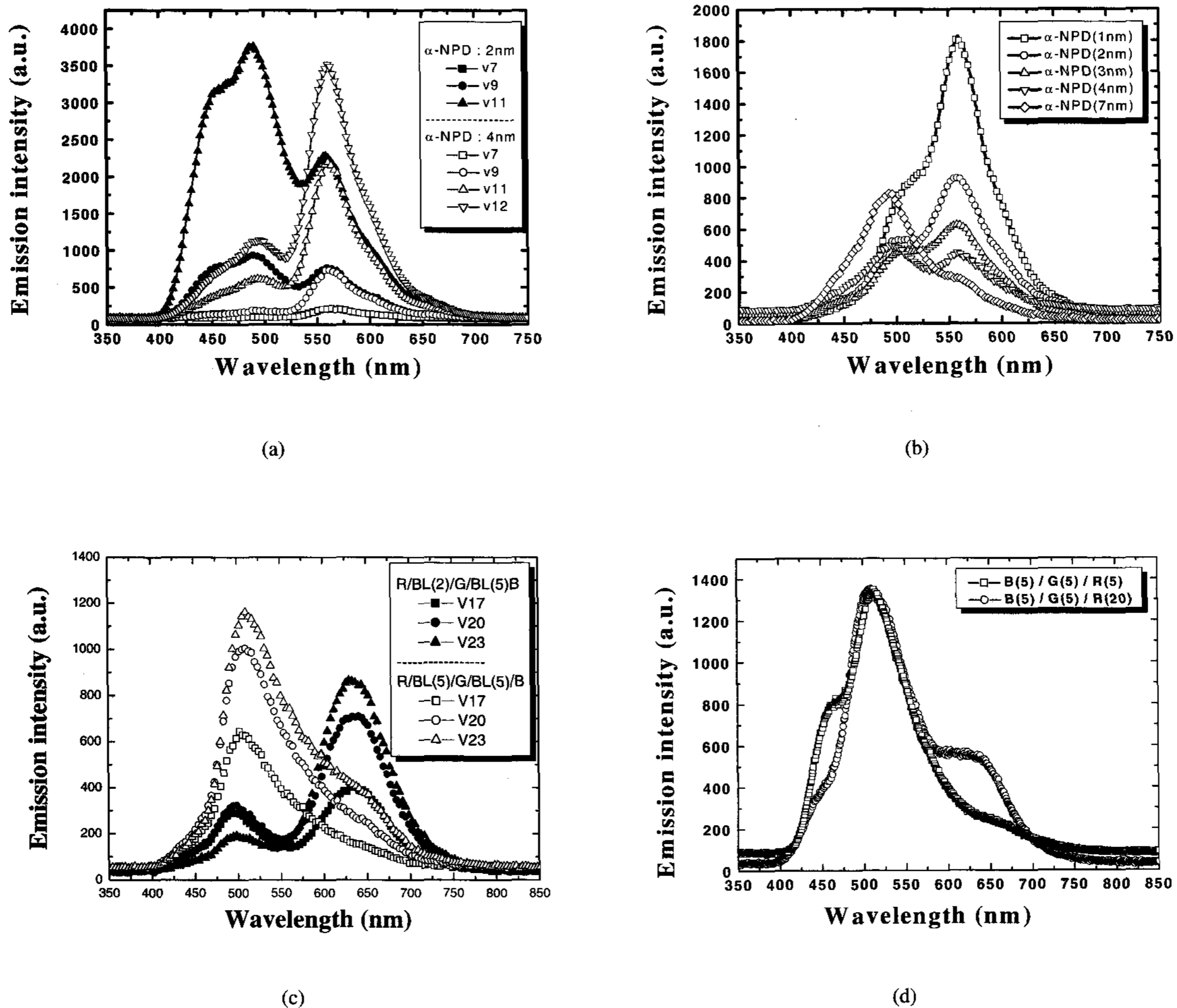


Fig. 2. The Shift of CIE chromaticity coordinate at various applied voltages for white OLEDs (a) : yellow(15) / BL(2, 4) / blue(15), (b) : blue(5) / BL(1, 2, 3, 4, 7) / yellow(20) (c) : red(15) / BL(2,5) / green(15) / BL(5,5) / blue(15), (d) : blue(5) / green(5) / red(5, 20).

changed from yellow to blue with respect to the thickness of blocking layer such as in the case of Fig. 1 (a). The emission spectra are shown in Fig.2 (b). With very thin blocking layer the blue emission was found to be stronger than yellow. As the thickness of blocking layer increases, the spectra shift to the shorter wavelengths. However, the dependence of the resulting color on the operating voltage was found to be quite different. As shown in Fig. 4 (b), the white emission was obtained at the thickness of blocking layer of 4nm. The emission color did not change even though the operating voltage increased. The non-sensitivity of this device structure to the operating voltage is not clear at this moment, but it is presumed that the degree of carrier blocking by the blocking layer could be perfectly

matched with the difference in mobility of electrons and holes in the emission layers, thus compensating for the degree of division of recombination zone.

The structure shown in Fig. 1 (c) is basically the same as that in Fig. 1 (a) except that no blocking layer was used. As mentioned earlier, the light emission was expected to occur around the blue emission region. In case of the very thin blue emission region with a much thicker yellow emission region, as in Fig. 1 (c), we expected that there would be a bigger contribution of yellow emission to the resulting emission, since it is well known that the light emission is originated from the region around 15-20 nm from the HTL-ETL interface. The CIE coordinates of the resultant emission are shown as bold symbols in Fig. 4 (b). At low operating voltages,

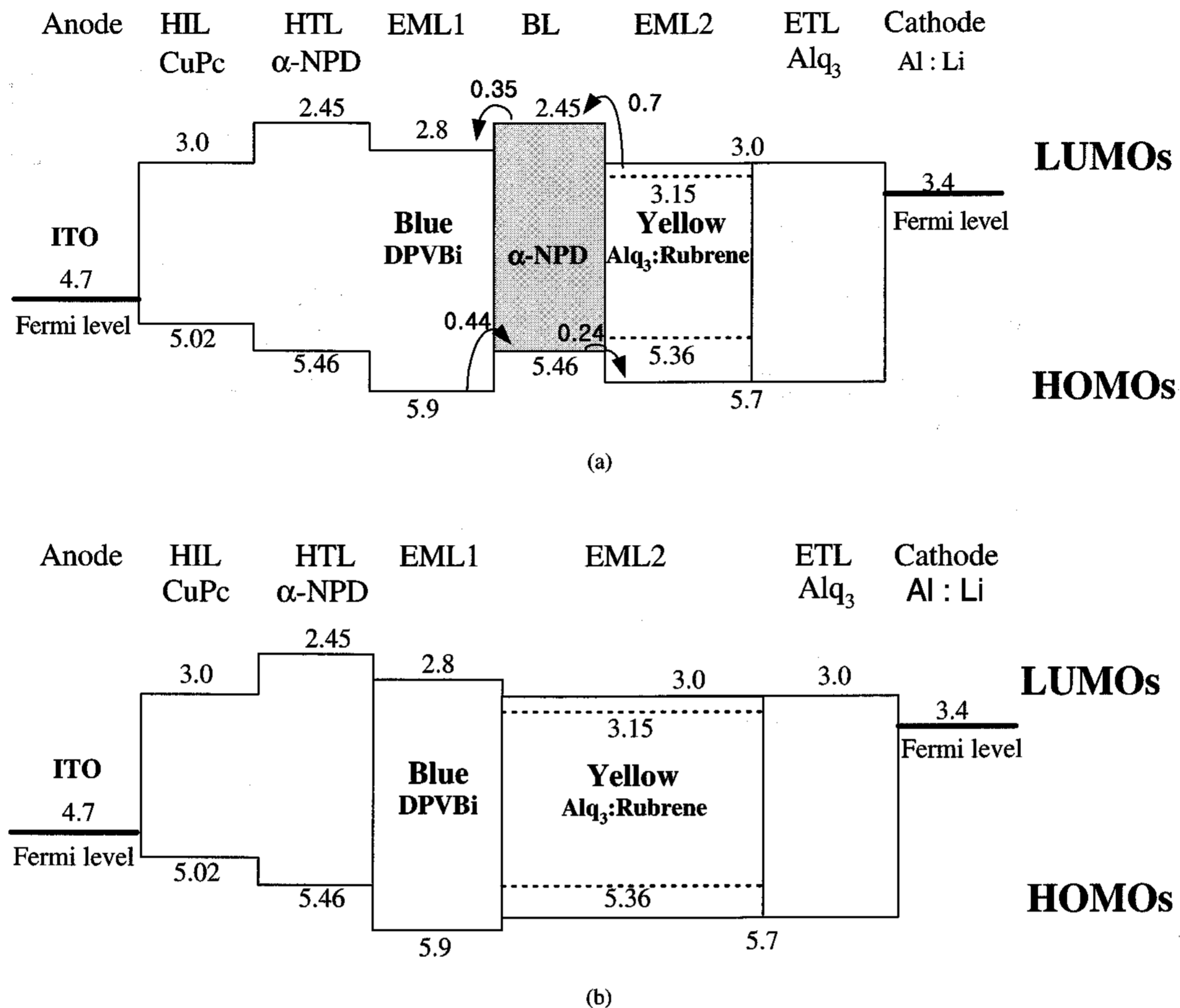


Fig. 3. The estimated energy band diagram [15, 16] for fabricated OLED structure. (a) : blue(15) / BL(4) / yellow(15), (b) : blue(5) / yellow(20).

the coordinates were observed to be close to the yellow color. At higher voltages, however, the emission shifted close to the white color. This means that it is possible to achieve the white emission without using a blocking layer, even though the emission color changes appreciably with the applied voltage. Since the three structures mentioned above used the two colors of yellow and blue to obtain the white emission, the red emission above the wavelength of 600 nm was very weak. In order to achieve full color display from the white emission, the red emission must be strong enough.

The structure shown in Fig. 1 (e) is composed of three different color emission layers and two blocking layers. Depending on the thickness of blocking layers, it is possible to achieve the white emission by direct color mixing. The emission spectra from the structure were shown in Fig. 2 (c). As can be seen from the spectra, the red emission became much stronger. In the case of thin blocking layer between the red and green emission layers,

the red emission was found to be stronger since the electron tunneling through the thin blocking layer was easier. However, the color emitted from the structure changed dramatically as the operating voltage changed. At low voltages the blue emission dominated, but the color tended to shift to green or red as the voltage increased.

Similar to the structure shown in Fig. 1 (c), a structure with three different color emitting layers and non blocking layer was fabricated and tested. The three emitting layers was in the order of blue, green and red starting from the anode side. In case of the three emitting layers with the thickness of 5 nm, the resulting color emitted from the structure was close to blue since most of the emission came from the HTL-ETL interface. In order to obtain a red shift of the emission, the thickness of red layer was increased to 20 nm. Since the total thickness of emission region was increased, it was expected that the exciton recombination zone would

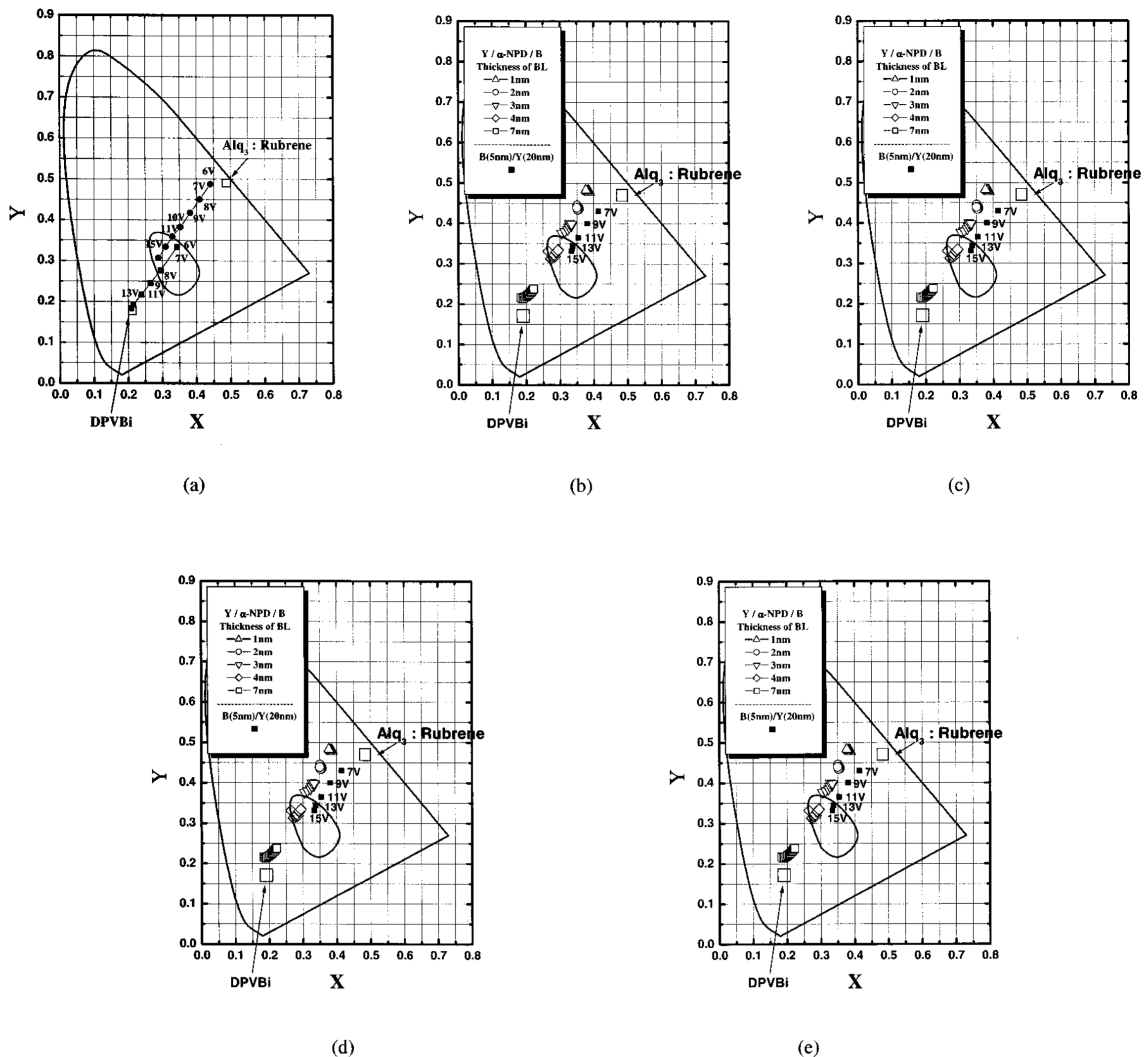


Fig. 4. EL emission spectra at various applied voltages for white OLEDs.

move back to the cathode side and the red emission from the thick red emission layer would contribute to the resulting emission. As shown in Fig. 2 (d), the resulting emission spectrum showed an increase in red emission strength in case where a thick red emission layer is used. When the thickness of red emission layer increased from 5 nm to 20 nm the CIE coordinates of the emission originated from the white region. As can be seen from the figure, the variation in the coordinate upon the driving voltage was found to be less than that in the case of blocking layers used. It has been demonstrated that the white emission could be obtained in various ways, such as two color structure, two color structure with a blocking layer, three color structure, and three color structure with two blocking layer. It should be noted here

that with a special structure, such as Fig. 1 (b), a voltage insensitive white emission is possible, which is desirable for the stable operation of the white OLED device.

The maximum luminescence of the structure shown in Fig. 1 (b) was 2,000 cd/m² and the power efficiency was measured to be 1.15 lm/W. In case of the white organic light emitting devices using three colors the luminescence efficiency was normally lower than that of devices with two colors. It should be mentioned that the efficiency of devices with three emission layers could be further improved as the optimization of the devices has not yet been explored. Further optimization of the device structure in order to achieve the white emission is in progress.

4. Conclusions

White organic light emitting devices in this work studies for various structures with multiple-color emitting layers and blocking layers. It has been demonstrated that the white emission could be obtained in various ways such as two color structure, two color structure with a blocking layer, three color structure, and three color structure with two blocking layer. It has been found that there is a trade-off in that the devices with three color emitting layers do not show high luminescence efficiency compared to those with two color emitting layers but show distinct red emission in the resultant emission spectra. The highest power efficiency achieved was measured to be 1.15 lm/W at 2,000 cd/m² for a structure with two color emitting layers.

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