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High Efficiency Red Phosphorescent Organic Light Emitting Diodes with Single Quantum Well Structure

JUNG SOO PARK,[1] TAE JIN PARK,[1] WOO SIK JEON,[1] GYEONG HEON KIM,[2] JAE HYUNG YU,[1] MYUNG JIN LIM,[1] AND JANG HYUK KWON[1]

[1]Department of Information Display, Kyung Hee University, Seoul, Korea
[2]Department of Chemistry, Kyung Hee University, Dongdaemoon-gu, Seoul, Korea (ROK)

We report highly efficient red phosphorescent organic light-emitting diodes with a triplet p-i-n single quantum well (QW) structure. This p-i-n single QW structure is realized using p-doped and n-doped wide band-gap hole and electron injection and transporting layers with narrow band-gap host and dopant materials. The maximum current and power efficiencies of 11.1 cd/A and 14.4 lm/W, respectively, are demonstrated by a good carrier confinement effect of QW. Very low driving voltage characteristics of 3.7 ~ 3.9 V at 1000 cd/m^2 are realized by almost no injection barrier with high conductivity configuration in our p-i-n structure.

Keywords Exciton confinement; narrow band-gap; organic light-emitting diode; phosphorescence; quantum well; wide band-gap

Introduction

Organic light-emitting diodes (OLEDs) have been commercialized as a technology for new flat panel displays and it considers as potential future lighting owing to their many attractive attributes such as thin feature, flexibility and low power consumption. In particular, phosphorescent OLEDs (PHOLEDs) are of considerable interest in recent years because singlet and triplet excitons can contribute to the emission of photons [1–3]. Nevertheless, PHOLEDs still have to overcome high driving voltage, high roll-off and short lifetime issues. The p- and n-type chemical doping techniques have been considered to reduce the operating voltage of phosphorescent OLEDs [4–7]. Such chemical doping with either electron donors or electron acceptors materials can significantly reduce the voltage drop across these films [8–11]. Earlier, the maximum power efficiency of 10.6 lm/W and a luminance of 100 cd/m^2 at 3.0 V with a power efficiency of 10.6 lm/W in red phosphorescent p-i-n OLEDs had been

Address correspondence to Prof. Jang Hyuk Kwon, Department of Information Display, Kyung Hee University, #1 Hoegi-dong, Dongdaemoon-gu, Seoul 130-701, Korea (ROK). Tel.: (+82)2-961-0948; Fax: (+82)2-968-6924; E-mail: jhkwon@khu.ac.kr

reported [12]. Even though this p-i-n technology has provided very good voltage characteristics, high quantum efficiency characteristics together with low driving voltage are not reported in red PHOLEDs to date. In order to achieve very good high efficiency in OLEDs, carrier confinement and/or exciton confinement technologies by the excition blocking layer, hole and electron blocking layers, and triplet quantum well (QW) configuration have been proposed. Among of them, excition blocking layers and hole and electron blocking layers were reported by several groups [13–15]. Few QW structures have been reported until now [16–17].

Generally wide band-gap host materials are very common in PHOLEDs because of a big splitting energy from singlet to triplet state. The spin exchange energy in general organic materials is very high as over 0.5 eV. Such high exchange energy prohibits making good carrier and triplet exciton confinements in the emissive layer (EML). Recently, a narrow band-gap host material of bis(10-hydroxybenzo[h] quinolinato)beryllium complex ($Bebq_2$) had been reported by our group [18]. This host has only ~0.3 eV singlet-triplet exchange energy. Such host materials can give us easier QW device design for the confinements of excitons and carriers in the EML. In this work, we demonstrate a p-i-n single QW structure using a $Bebq_2$ host and the chemical doping technique to wide band-gap hole and electron transport layers in the red PHOLEDs. High efficiency and low driving voltage characteristics with this structure are reported herein.

Experimental

To make p-i-n singe QW devices, sublimated $Bebq_2$, 4,4′,4″-tri(N-carbazolyl)triphenylamine (TCTA), bis[2-(2-hydroxyphenyl)-pyridine] beryllium ($Bepp_2$) and tris (1-phenylisoquinoline)-iridium ($Ir(piq)_3$) were purchased from Gracel Corporation and Luminescence Technology Corporation. We have fabricated several red PHOLEDs with ITO (indium-tin-oxide)/30% WO_3 doped TCTA (60 nm)/TCTA (10~12 nm)/$Bebq_2$:$Ir(piq)_3$ (10~12 nm)/$Bepp_2$ (10~12 nm)/Cs_2CO_3 doped $Bepp_2$ (20 nm)/LiF (1 nm)/Al (100 nm) structure. (See Fig. 1) Devices were fabricated as following procedures. The sheet resistance of ITO substrates was about 12 Ω/sq with 150 nm thickness. The ITO substrates of 2.5 cm × 2.5 cm were cleaned by ultra sonic in deionized water and isopropylalcohol in sequence. Later, substrates were dried in

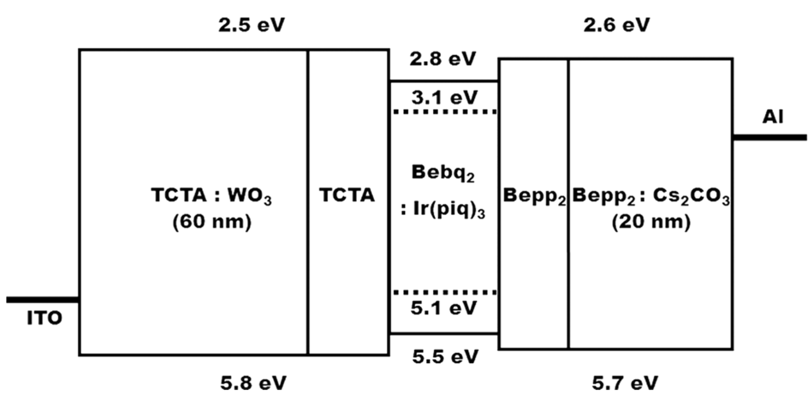


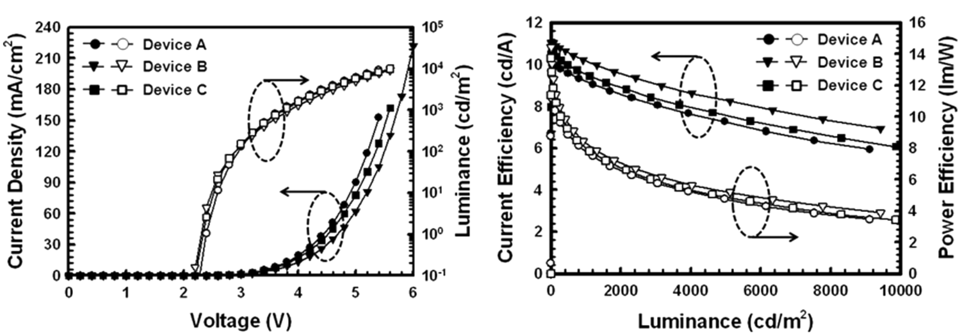
Figure 1. The energy band diagram of p-i-n single QW red PHOLEDs.

air. Finally, UV ozone treatment of substrates was done in a chamber before loading into an evaporation chamber. The organic layers were deposited onto an ITO coated glass substrate in a multi-chamber vacuum system at a pressure of 1.0×10^{-7} Torr. The TCTA doped with WO_3 (doping concentration 30 wt%) serves as the p-doped hole transporting layer (HTL). A layer of $Bepp_2$ doped with Cs_2CO_3 serves (doping concentration 10 wt%) as the n-doped electron transporting layer (ETL). Organic layers are controlled independently using separate quartz thickness monitors. $Bebq_2$ and $Ir(piq)_3$ was used as a narrow band-gap host and a dopant material, respectively. The emission area was 4 mm^2 in all devices. The current density-voltage (J-V) and luminance-voltage (L-V) characteristics of red PHOLEDs were measured with a Keithley SMU 238 and Minolta CS-100A. Electroluminescence (EL) spectra and CIE color coordinate were obtained by a Minolta CS-1000A.

Results and Discussion

Figure 1 shows our device configuration of p-i-n single QW devices. Wide band gap charge transporting materials having high triplet energies with high LUMO (lowest unoccupied molecular orbital) energy levels are desirable to make p-i-n single QW structure in red PHOLEDs. The TCTA has been reported as an excellent host hole transporting material with a 2.7 eV triplet energy and a 2.5 eV high LUMO energy [19]. The 30% WO_3 doped TCTA layer exhibits Ohmic-like J-V characteristics with very good conductivity of $\sim 10^{-5}$ S/cm. As consequences, the 30% doped TCTA was used as a hole injection layer. The TCTA also used as the buffer layer to give a good triplet exciton confinement effect without any injection barrier in the EML. For an n-doped ETL layer, Cs_2CO_3 doped in $Bepp_2$ was used. The $Bepp_2$ also has a high triplet energy of 2.7 eV. Similar conductivity results ($\sim 10^{-5}$ S/cm range) in doped $Bepp_2$ were observed. The $Bepp_2$ was used as the n-doped electron injection and buffer layer in our single QW structure.

In this work, we have fabricated three red p-i-n single QW PHOLEDs to optimize EML and buffer layer thickness, respectively. Figure 2 shows the device characteristics of single QW red PHOLEDs with different EML thickness. Device A and B were made with 10 nm and 12 nm EML and the same 12 nm buffer layer thickness, respectively. Device C was made with 12 nm EML and 10 nm buffer layer thickness.



(a) (b)

Figure 2. Device performances of fabricated red PHOLEDs. (a) J-V-L characteristics (b) current and power efficiency-luminance. (Device A: 10 nm EML and 12 nm buffer layer, Device B: 12 nm EML and 12 nm buffer layer, Device C: 12 nm EML and 10 nm buffer layer.)

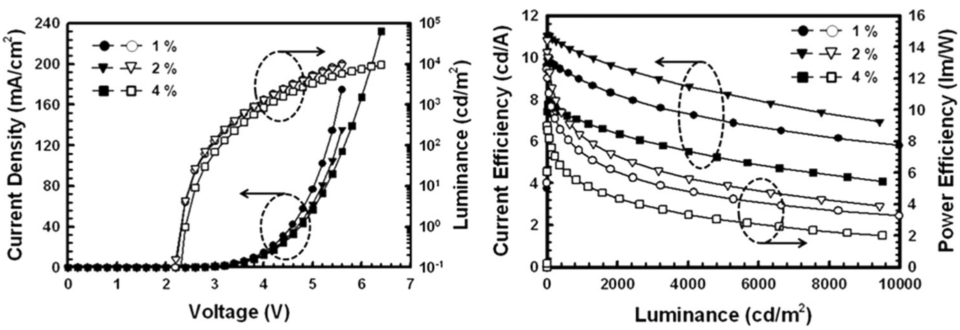
The doping concentration was fixed as 2 wt% in Device A∼C. All devices were measured until 10,000 cd/m^2 brightness value. The driving voltages (at 1000 cd/m^2) are 3.7 V for Device A and 3.8 V for Device B, respectively. The maximum current and power efficiency are 9.9 cd/A, 11.4 lm/W for Device A and 11.1 cd/A, 14.4 lm/W for Device B, respectively. The operating voltage in Device B was increased about 0.2 eV with increasing EML thickness. However, Device B shows good current and power efficiency improvement. The external quantum efficiency (EQE) of this device is 13.2%, which is the highest value compared with the previous report of 12.2% EQE [12]. The increase of additional EML thickness does not provide any additional quantum efficiency enhancement. The optimum EML thickness is 12 nm in our p-i-n single QW devices.

To reduce driving voltage more, Device C was designed with thinner thickness (10 nm) of TCTA and $Bepp_2$ buffer layers at the fixed EML thickness of 12 nm. The driving voltage (at 1000 cd/m^2) of Device C is 3.7 V. The maximum current and power efficiency are 10.6 cd/A, 13.7 lm/W for Device C, respectively. As reducing buffer layer thickness, driving voltage is improved about 0.2 V. However, device efficiency is decreased about 6% due to exciton quenching by metal oxide doped layers. As a result, we conclude that the best thickness of buffer layer is 12 nm in our p-i-n single QW structure. Table 1 summarizes the performances of all devices.

Furthermore to optimize the p-i-n single QW structure, we have fabricated red PHOLEDs with different doping concentrations (1%, 2%, 4%). The device characteristics of these red PHOLEDs with different doping concentrations are presented in Figure 3. The turn-on voltages (1 cd/m^2) with different doping concentrations are 2.3 V for 1%, 2.3 V for 2% and 2.4 V for 4%, respectively. The driving voltage to reach 1000 cd/m^2 is 3.9 V for 1%, 3.9 V for 2%, and 4.1 V for 4%, respectively. The maximum current efficiency are 9.9 cd/A for 1%, 11.1 cd/A for 2% and 7.8 cd/A for 4%, respectively. The maximum power efficiencies are 12.5 lm/W for 1%, 14.4 lm/W for 2% and 8.9 lm/W for 4%, respectively. The best EL performance is obtained in 2% doping concentration among these three p-i-n single QW red PHOLEDs, indicating that 2% condition has the best charge balance in the emitting layer. The CIE coordinates at 1,000 cd/m^2 with different doping concentration shows the same value as CIE (0.66, 033), indicating almost complete energy transfer from the narrow band gap $Bebq_2$ host material to the $Ir(piq)_3$ dopant. All devices show very good deep red color coordinates. However, 1.0% doping concentration shows a week host emission at about 504 nm, indicating that a 1.0% doping concentration is the minimum possible doping concentration.

Table 1. The device performances of p-i-n single QW red PHOLEDs

	Device A	Device B	Device C
Turn on voltage (@ 1 cd/m2)	2.3 V	2.3 V	2.4 V
Operating voltage (@ 1000 cd/m2)	3.7 V	3.8 V	3.7 V
Efficiency (@ 1000 cd/m2)	9.1 cd/A	10.2 cd/A	9.4 cd/A
	7.5 lm/W	8.5 lm/W	7.8 lm/W
Maximum efficiency	9.9 cd/A	11.1 cd/A	10.6 cd/A
	11.4 lm/W	14.4 lm/W	13.7 lm/W
Maximum EQE	11.8%	13.2%	12.6%



(a) (b)

Figure 3. Device performances of fabricated red PHOLEDs with different doping concentration; (a) J-V-L characteristics (b) current and power efficiency-luminance.

Interesting results on the performance of our p-i-n single QW device configuration have been obtained. As the p-doped hole injection layer, hole injection from ITO has almost no barrier. Injected holes from the hole injection layer can transport easily to the 5.8 eV HOMO (highest occupied molecular orbital) level of buffer layer. Barrier to hole injection into an EML is negligible. Also, electrons injected from the cathode move freely into the EML to the LUMO level (2.8 eV) of dopants and finally generated triplet excitons give rise to good the phosphorescent emission. Figure 4 shows the potential model describing the single QW structure with TCTA and $Bepp_2$ buffer layers. The HOMO and LUMO level of TCTA and $Bepp_2$ were 5.6 eV, 2.5 eV and 5.7 eV, 2.6 eV, respectively. The TCTA and $Bepp_2$ buffer layer have high LUMO and deep HOME levels compare to the $Bebq_2$ host layer. The TCTA and $Bepp_2$

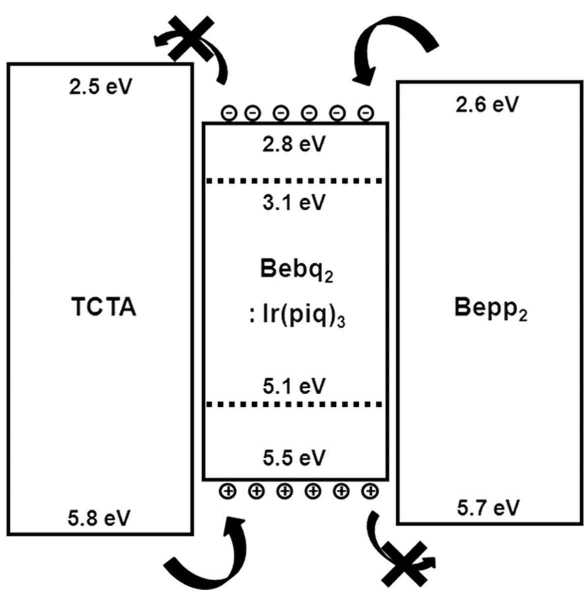


Figure 4. The potential model describing a single QW structure with TCTA and $Bepp_2$ buffer layers in the red PHOLEDs.

buffer layers can confine electrons and holes in the EML. Therefore, the red PHOLEDs with p-i-n single QW structure improved the recombination efficiency and driving voltage significantly.

Conclusions

We propose a p-i-n single QW structure with wide band-gap hole and an electron transporting layers, narrow band-gap host, and red dopant materials. Our p-i-n single QW configuration of red PHOLEDs could confine the triplet excitons in the EML and provide no injection barriers with high conductivity. High current and power efficiency values of 11.1 cd/A and 14.4 lm/W in p-i-n single QW red PHOLEDs are demonstrated with 12 nm TCTA and $Bepp_2$ buffer layers and 12 nm EML. This p-i-n QW configuration is applicable to future OLED display and lighting applications.

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