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Color stable phosphorescent white organic light-emitting diodes with double emissive layer structure

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ABSTRACT

In this paper, we report color stable phosphorescent white organic light-emitting diodes (OLEDs) based on a double emissive layer (EML) structure composed of blue and red/green phosphorescent units. Deep hole trapping situation of red and green dopants at the red/green EML could induce less voltage dependent white spectral characteristics by restricting the change of exciton generation zone. A wide band-gap host material, 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy), was used for achieving such deep-trap generation. Fabricated phosphorescent white OLED shows a slight color coordinate change of (−0.002, +0.002) from 1000 cd/m^2 to 5000 cd/m^2 with power efficiency of 38.7 lm/W and current efficiency of 46.4 cd/A at 1000 cd/m^2. In addition, negligible color changes were observed by delaying red dopant saturation time using optimum red dopant concentration.

1. Introduction

White organic light-emitting diodes (WOLEDs) have shown strong potential possibilities as next generation solid-state light sources due to their promising properties such as spatially homogeneous white emission across the surface of large-area and are eco-friendly. There are several requirements for WOLEDs to be used as solid-state luminaire, such as high efficiency, high color rendering index (CRI), proper color coordinates, long lifetime, high color stability etc. [1,2]. There have been reports on various fabrication approaches of WOLEDs to fulfill all these requirements. Among of them, mainly three categories according to the architecture of emissive layers (EMLs) could be defined. The use of multiple emitters within a single EML is the first way [3–6]. A second is to use multiple adjacent EMLs and tandem stacks with two or three color combinations are the third one [7–12]. The first and second methods are more suitable for the mass production than the third one due to their simplicity of fabrication. However, these show a poor color stability problem as voltage variation because of the changes in emission zone and/or energy transfer situation. When two or three different phosphorescent emitters are close to each other within Dexter radius, sequential energy transfer from higher triplet to lower triplet state occurs until neighbor lower energy state of dopants are fully excited. After full excitation of lower energy state of dopants at the high current density, higher triplet state dopants contribute more for the light generation. Therefore, color shift from red to green or blue as the voltage increase is generally observed in such as single and multi-EML devices. Even in single EML structure, there is some color variation with the voltage increase if the dopant ratio among three dopants is not an optimum condition [3,13–16]. Normally, we could drastically reduce the voltage dependent spectral changes of single EML device by using the doping concentration of a lower band gap emitter as low as possible, about 0.1–1.0% [17,18]. In addition to this color change issue related by energy transfer, the change of exciton generation zone also gives rise to color shift as the voltage increase in many multi-EML cases.

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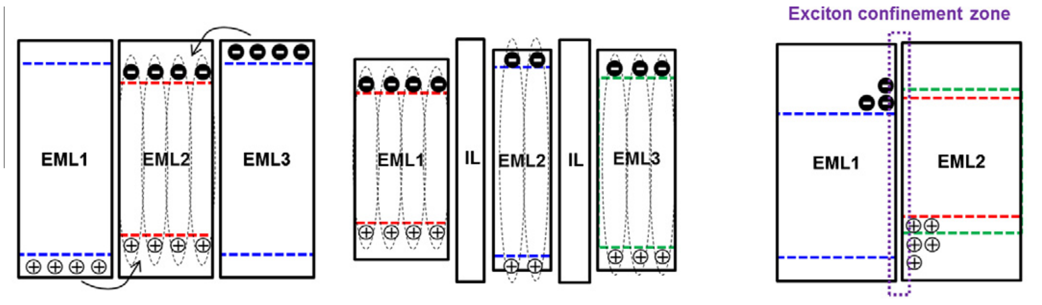
The different field dependency between hole mobility of hole transporting layer (HTL) and electron mobility of electron transporting layer (ETL) and/or different carrier trapping situation at the EML move exciton emission zone with increasing voltage in multi-EML structure. From the color stability perspective, blue/orange complementary colors WOLEDs are better than three primary colors (red, green, and blue) WOLEDs. The blue/orange complementary colors has only one energy transfer path from blue to orange dopant that is easier to determine the optimum values of doping concentration, while three color system has at least three energy transfer paths (blue to green dopant, blue to red dopant, and green to red dopant), therefore it is more difficult to control the emission balance and optimum concentrations. However, three color system is more favorable for high CRI [3,13]. To date, many efforts are under way to improve the color stability in multi-EML white devices.

Fig. 1 shows several reported concept of device structures to have good color stability in multi-EML WOLEDs. The first concept has the low band gap emitter between high band gap emitters [19–21]. Quantum well type energy band could restrict carrier movement and exciton zone effectively at the center of emitting layer, which results in good color stability characteristics. This structure is quite good for two color WOLEDs, but not for three color WOLEDs because three color emitters do not have large energy difference. The second method is to insert the interlayer(s) between different emitting layers [22–25]. This interlayer could control balanced hole and electron movement regardless of voltage increase. It also helps to keep exciton formation zone without any variation by blocking energy transfer between different EMLs or effectively transferring triplet exciton energy to different EML layers. So far, there are so many papers based on this concept. Unfortunately, such additional use of the interlayer(s) is not good for the mass production. The third concept is to use adjacent two EMLs with deep charge trapping situation at the one of EMLs. As shown in Fig. 1, deep hole trapped carriers could restrict hole carrier and exciton movement. Hence it can achieve stable WOLEDs. There was a report of similar device structure, however, color stability is not so excellent because they did not fully utilize this concept [26].

In this paper, we demonstrated color stable phosphorescent WOLEDs with the deep hole trapped double emitting layer structure. The fabricated devices with this concept shows slight color coordinates change of ($\leqslant$0.002, $\leqslant$0.002) from 1000 cd/m^2 to 5000 cd/m^2. Power efficiency of 38.7 lm/W and current efficiency of 46.4 cd/A at 1000 cd/m^2 are achieved in this optimized device. Additional negligible color changes were induced by delaying red dopant saturation time using optimum red dopant concentration.

2. Experimental

The sublimated grade di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) were purchased from Luminescence Technology and were used as the HTL and host material, respectively. Twice sublimated 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) from Daejoo Electronic Materials were used as an ETL. Dipyrazino[2,3-f:2′,3′-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) and bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic) from Luminescence Technology were used as the HTL and blue phosphorescent dopant material, respectively. (Tris(2-phenylpyridine)iridium) (Ir(ppy)$_3$) from Gracel (now Dow Chemical company) was used as a green phosphorescent dopant material. A red phosphorescent dopant material iridium(III)bis(4-methyl-2-(3,5-dimethylphenyl)quinolinato-N,C2′)acetylacetonate Ir(mphmq)$_2$(acac)) was synthesized by our reporting method [27]. Fig. 2 shows the chemical structures of all organic materials used in the device fabrication. To fabricate WOLED devices, we used a clean glass substrate coated with a 150 nm thickness of ITO layer having a sheet resistance 10 Ω/square as an anode. The active patterns size of 2 × 2 mm^2 were formed by the photolithography and wet etching processes. The ultrasonic cleaned glass substrate in an isopropyl alcohol, acetone, and methanol was rinsed in deionized water, and finally treated in ultraviolet (UV)-ozone for 3 min. The ozone gas was generated using UV light to excite the oxygen in the air inside the chamber. Each organic layer was deposited under a pressure of $\sim$10^{-7} torr with total deposition rate of $\sim$0.5 Å/s. Subsequently, 0.5 nm thickness of lithium fluoride (LiF) and



Multi-EML with quantum well structure Multi-EML with interlayers Double-EML with charge trapping structure

Fig. 1. Emission zone configurations for color stable WOLEDs.