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Adjusting dopant concentrations in solution process to optimize the white phosphorescent organic light-emitting diodes

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ABSTRACT

In this study, white phosphorescent organic light-emitting diodes (PhOLEDs) have been demonstrated with small molecule by using solution processes. Spin-coating is employed as the way for deposition method. 4,4′-N,N′-dicarbazole-biphenyl (CBP) which is typical small molecule based ink is used for spin-coating method, and three phosphorescent dopants materials, Firidium(III) bis[(4,6-difluoro phenyl)-pyridinato-N,$C^{2\prime}$] picolinate (FIrpic), bis[1-(phenyl) isoquinoline) iridium(III) acetyl acetonate ($Ir(piq)_2$ (acac))], and iridium(III) tris(2-phenylpy-ridine) ($Ir(ppy)_3$) were prepared. For spin-coating processes, various parameters properties were investigated including materials concentrations, solvents effect, and electron transporting materials to get high efficiency and white color of white PhOLED device. As a result, the precisely controlled solution processes could be a promising technology for solution process can be a good alternative of vacuum deposition technology.

1. Introduction

White organic light-emitting diodes (OLEDs) have attracted much interest because of their potential application in full color display, backlights for liquid crystal displays and solid lighting sources [1–3]. There are two approaches to fabricate OLEDs based on the materials employed: thermal vapor deposition and solution-based process. Although the vacuum-deposition processes are far ahead of the solution processes from the commercialization point of view, the solution processes for the fabrication of OLEDs are still fascinating due to their potential advantages for the production of large area devices at low cost [4,5]. However, thermal vapor deposition process under high vacuum increases fabrication complexity and makes the utilization of the expensive OLED materials [6]. In addition, making multi-dopants OLEDs, such as white OLEDs, needs precise control of the doping concentration of each dopant in the emitting layer (EML) to obtain the emission in desired wavelength [7–8]. It makes the fabrication process much harder and greater complexity in vacuum process. As an alternative approach, the best way to overcome these drawbacks is to use solution process for the fabrication of OLED [9]. For example, spin-coating or ink-jet printing for polymers have been well studied since 1990 [10] and screen printing [11] can be effectively used to fabricate large-area, high-resolution full-color flat-panel displays [12,13]. This technology is mainly focused in reducing manufacturing costs as well as to improve procedures for mass-production lines [14]. A cost reduction in multilayer devices is anticipated when at least some of the OLED layers can be prepared from solution.

By definition, white emission requires the mixture of complementary (i.e., blue and yellow or orange) or primary colors (red, green, and blue) [15]. Naturally, an emitting layer with precise ratios of multiple components is easier to achieve by solution process, which overcomes the difficulties of co-evaporation and accurately doping performed by vacuum-deposition process. Recently, numerous works about the WOLEDs by solution-processing small molecules have been reported [16–18], but the comprehensive performances of the devices need to be further improved. Hou et al. reported a WOLEDs based on the mixed-host materials [16], but their power efficiencies were not more than 15.6 lm/W. Zhang et al. reported a solution-processed of WOLED with high efficiency based on a dendritic host [17], but its color rendering index (CRI) was still too low (less than 65). Liu et al. reported a WOLED exhibited efficient white emission with Commission Internationale de l' Eclairage (CIE) coordinates of (0.33 and 0.34) [19]. However, the main difficulty in building multilayered devices using solely a solution process, since the processing of a new layer

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will inevitably affect the underlying layer [20]. Among solution processes, spin-coating process which conventionally used in solution process was chosen. Spin-coating is the method that an excess amount of a solution is placed on the substrate, which is then rotated at high speed of round per minute (rpm) in order to spread the fluid by centrifugal force and it is widely known for solution coating process. There are a lot of parameters which determine device performance in spin-coating process such as solvent, material, process and fabrication environment. Among many variables which can affect device property, we decided to concentrate solvent, dopants concentration, and electron transport material to know the effect of each parameter in blue and white PhOLEDs with spin-coating process.

In this paper, starting from a blue device structures with a solution-processed were fabricated, whose hole-injection layer (HIL) and EML are fabricated by spin-coating with vacuum-deposited electron transport layer. Blue PhOLEDs with different solvent solutions and dopants concentrations were investigated. Furthermore, white PhOLEDs solution process with three-color dopants was also fabricated. In these devices, the dopant materials concentrations and electron transport layer were studied. Our result shows a possible approach to achieve efficient and low-cost small-molecule based white PhOLEDs, which avoids the complexities of the co-evaporation process of multiple dopants in host materials of in vacuum depositions.

2. Experimental

In the experiment, poly-3,4-ethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) is used as HIL, 4,4′-N,N′-dicarbazole-biphenyl (CBP) recognized to have bipolar transport character was used as host materials in the present work, and three phosphorescent dopants materials, Firidium(III) bis((4,6-difluoro phenyl)-pyridinato-N,$C^{2\prime}$) picolinate (FIrpic), bis(1-(phenyl) isoquinoline) iridium(III) acetyl acetonate ($Ir(piq)_2$ (acac)), and iridium(III) tris(2-phenylpy-ridine) ($Ir(ppy)_3$) for blue, red, and green dopants, respectively, tris(8-hydroxy-quinoline)aluminum (Alq_3) and 1,3,5-tris(N-phenylbenzimidazol-2-yl) benzene (TPBi) as electron transport layer (ETL), and LiF/Al as cathode. The structure of resulting devices is ITO/PEDOT:PSS (HTL)/CBP:dopant(s) (EML)/Alq_3 or TPBi (ETL)/LiF/Al. The schematic energy-level diagram of all materials is shown in Fig. 1.

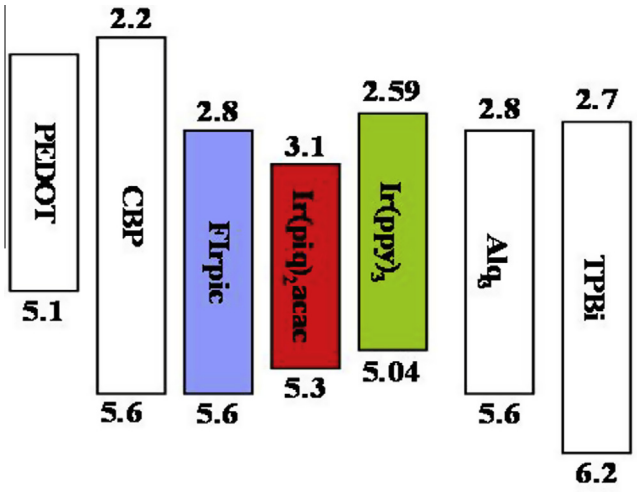

Fig. 1. Schematic energy band diagrams of the blue and white PhOLEDs materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The Indium-tin-oxide (ITO) substrates are sufficiently cleaned by ultrasonication in acetone, isopropyl alcohol and deionized water before being placed into oven for 10 min to dry out. These substrates are further treated with oxygen plasma prior to use. PEDOT:PSS mixture was spin-coated onto the ITO coated glass substrate at spin speed of 3500 rpm. The samples are then kept in an oven at 100 °C for 50 min to remove the residual solvent. The blue PhOLEDs light-emitting layer was prepared by mixing host and dopant solution, the ratio of CBP:FIrpic was 1.5:0.5 wt% in chlorobenzene (CB) and 1.5:0.5, 1.6:0.4, and 1.7:0.3 wt% in toluene (TL). For the white PhOLEDs, the light-emitting layer was also prepared by mixing host and dopants solution, CBP:FIrpic:$Ir(piq)_2$ (acac):$Ir(ppy)_3$ in toluene (TL) via various concentrations. In the blend system of the white PhOLEDs, CBP:FIrpic:$Ir(piq)_2$ (acac):$Ir(ppy)_3$, the ratio of CBP:FIrpic was fixed at 1.6:0.4 and the ratio of $Ir(piq)_2$(acac):$Ir(ppy)_3$ was tuned. The ratios of $Ir(piq)_2$(acac):$Ir(ppy)_3$ were 0.0125:0.0125. The ratios of $Ir(piq)_2$ (acac) was 0.025 and 0.0125. The EML solution was spin-coated onto HIL layer using spin-coating speed of 4000 rpm for 30 s to give a light-emitting layer, and samples were then baked on a hot plate at 100 °C for 10 min to remove the remaining solvent. The spin-coating and baking processes were carried out in a nitrogen atmosphere glove box [21]. Subsequently, the samples coated with HIL and the EML were loaded into organic chamber, the 40 nm thick of Alq_3 or TPBi as ETL was deposited by vacuum thermal evaporation. Finally, a thin layer of LiF (0.6 nm) and Al (150 nm) were evaporated to form the cathode and complete the devices. The emission area of devices was 0.5 × 0.5 mm.

The current–voltage-luminescence characteristics are measured with a Keithley 2400 source meter. EL spectra and CIE coordinates of the devices are analyzed via a spectrometer (PR650). All measurements are carried out under ambient conditions at room temperature.

3. Results and discussion

3.1. Effect of solvents and FIrpic concentrations for blue PhOLEDs

Nowadays, many research groups are focusing upon overcoming the limitations such as efficiency in spin-coating process and various approaches are proceeding. Meanwhile, investigation of each parameters which can affect film property or device performance is very meaningful. In spin-coating process, most of all, solvents of blend ink are very significant because they should have not only ability of dissolution for organic materials but also good film property which is comparable to vacuum-processed film. In order to confirm the effect of solvent, common organic solvents which are CB and TL were employed. To investigate device characteristics as changing solvent, we fabricated two samples which are spin-coated with CB and TL solvents. In order to compare solvent effect exactly, the layer of each samples are controlled in same spin-coated rpm, spin-coated times and concentration.

The blue PhOLEDs layer (CBP:Firpic) was dissolved in different solvents of CB and TL, which is CBP:Firpic concentration of 1.5:0.5 wt%. Fig. 2 shows the luminance and current density versus voltage characteristic of blue PhOLED in CB and TL solvents. From the inset in Fig. 2, we can easily find that current densities of TL device is higher than CB device, because using TL solvent can improve the chance for the charges to be directly injected to EML. However, the obvious luminance enhancement could not be found in the same current density, which resulted in the decrease in current efficiency of CB device due to the unbalance hole and electron recombination in EML. The high luminance of 435 cd/m^2 at 20 mA/cm^2 was obtained from TL solvent (242 cd/m^2 in CB solvent). Fig. 3 shows the current efficiency versus current density