White organic light-emitting diodes prepared by a fused organic solid solution method

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This letter demonstrates a white organic light-emitting diode (OLED) with high color stability fabricated by using a single organic white-emitting layer. The dopants were introduced prior to the device fabrication process through organic solid solution process formed by high-temperature and high-pressure fusion process. A high band gap organic material, α-naphthlyphenylbiphenyl diamine, was adopted and precisely doped with several kinds of fluorescent dyes as the emitting material. The most important benefits of using this fused organic solid-solution technique are the precise control of dopants, ultrauniform mixture of dopants in the host, easy fabrication; and, as a result, the fabricated white OLEDs show extremely little color shift with increasing injection current. The simplified device fabrication process is believed to be beneficial to the white OLED display and lighting industrialization. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1866216]

Organic light-emitting diodes (OLEDs) have aroused serious research interest from both academia and industry in the last two decades for their unique features in lighting and flat-panel display technologies.[1–3] Foremost among them white OLEDs have brought special attention for their potential applications in lighting, backlighting, and full color display.[4–6] The white electroluminance from the OLEDs can be a combination of the three primary colors from different doped organic materials, this in turn, requires multiemission layer structures.[7,8] Although it is, in general, possible to include one dopant and one host material for each emitting layer,[9,10] it is necessary to evaporate more than one emission layer in order to obtain white emission. It is possible to generate white light by a combination of only two different electroluminescences from organic layers as a result of the broad emission spectra of common organic emitters. The structure for the two-emission-zone white OLEDs is rather simplified, but the drawback is that the emission spectra cannot cover all the visible colors. In general, the fabrication of white OLEDs is relatively more complicated than that of other single color devices and the color stability is difficult to maintain since at least two precise controls of the dopant concentrations are required.

This letter reports a white OLED in which the single emission host material is uniformly doped prior to the evaporation process. The OLED structure is more simplified than those previously reported.[11–15] This new technology not only shows great convenience on device fabrication but also gives high device reproducibility.

Our approach is to utilize three or more kinds of dopants in one emission host material. This doping technique is easily realized by solution process in polymer involving systems, as in the case of the fabrication of polymer light-emitting diodes.[16] For small molecular systems, especially when some of them are extremely tiny, on the other hand, it is practically difficult to precisely control more than three components at the same time by thermal co-evaporation method. In order to avoid co-evaporation process, another method called "fused organic solid solution" processing is adopted to fabricate our white OLEDs.

The technology is that the host light-emitting material is mixed with several kinds of fluorescent dyes in their solid state with certain weight ratio before it is loaded into the vacuum system for evaporation. To effectively dope the host material, fusion process is expected to play a crucial step. We select α-naphthylphenylbiphenyl diamine (α-NPD) as the host material since its energy band gap is large enough compared to the blue dopants. Knowing in advance that many compounds used in OLEDs are easily sublimed, especially under low pressure (which sets a barrier for fusing process), a high-pressure system with inert gas protection to avoid decomposition is adopted to ensure the quality of the doped NPD. The dyes and undoped NPD were mixed and heated in a micro-reactor with high-pressure nitrogen gas. Figure 1 shows the schematic illustration of the experimental setup for preparing organic solid solution. The nitrogen pressure is above 250 psi and the fusion temperature is around 230 °C which was observed visually through the windows on the reactor.

In our material system, $4,4'$-Bis(2,2-diphenylethen-1-yl)biphenyl (DPVBi) is used for the blue emission dopant, 10-(2-Benzothiazolyl) -2,3,6,7 -tetrahydro -1,1,7,7, -tetra methyl-1H,5H,11H[1] benzopyrano[6,7,8-ij] quinolizin-11-one (C545T) for the green, 5,6,11,12-tetraphenylnaphthacene (rubrene) for the yellow, and 4-(dicyanomethylene)-2-tert-butyl -6-(1,1,7,7 -teramethyljulolidyl -9 -enyl)-4H-pyan (DCJTB) for the red. The corresponding weight ratio can be effectively adjusted by changing the weight of each component before they are mixed. Following the fusion process, a uniform doped NPD powder was subjected to thermal analysis by the differential scanning calorimeter (DSC). The thermal history is as follows: the doped NPD was first heated up to 300 °C and rapidly cooled down to room temperature at a speed of $\sim$50 °C/min. This amorphous solid was then heated up again at a speed of $\sim$5 °C/min and the DSC curve was recorded. The pure NPD heating curve was also obtained using the same procedure for comparison. Figure 2 shows the DSC heating curves of pure and doped NPD after
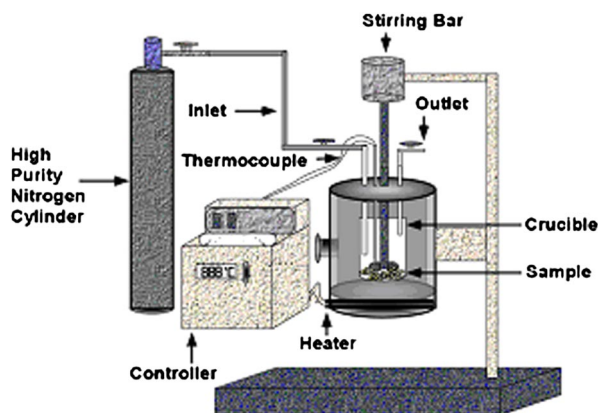
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FIG. 1. The schematic illustration of the experimental setup for preparing organic solid solution at high temperature and high pressure.

cooling down from 300 °C. The doped NPD sample consisting of NPD, DPVBi, C545T, rubrene, and DCJTB has the weight ratio of 100:4.12:0.282:0.533:0.415. For pure NPD, the glass transition temperature (T_g), crystallization transition temperature (T_c), and melting point (T_m) can be clearly identified by the features shown on the DSC curve. For the case of doped NPD, similar features which define the thermal phase transition temperatures can still be located on the DSC curve. The T_g for doped NPD is shifted to a little lower value than that of pure NPD. However, the T_c value is higher than that of pure NPD, so it is expected that the doped NPD should not be able to transform into the crystalline state easily, particularly at relatively high temperature. Both the pure and doped NPD share nearly the same melting temperature except the transition shape of the doped NPD is slightly broadened due to anharmonic interactions between pure NPD and the dopants. Similar molecular interactions in polymeric systems during phase transition have also been observed by using DSC.[17] In general, the thermal analyses of the two samples are similar and thus their thermal properties are alike. This characteristic is important in evaporating thin film from the doped material.

As shown in the inset of Fig. 3, our device structure consists of a hole blocking material 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) serving as the hole/exciton blocker between the electron transport material tris-

(8-hydroxyquinoline) aluminum (Alq_3) and the hole transporting material NPD. The doped NPD serves as the white light-emitting material. As stated before, the selection of the right weight ratio of the four kinds of fluorescent dyes is crucial to the quality of the white light emission. The weight ratio was empirically obtained by tracking the chromaticity coordinates and emission spectra from different doped NPD devices. The insufficiency of a particular primary color can then be compensated by adjusting the relative weight ratios of the dye components. The right weight ratio we obtained for NPD, DPVBi, rubrene, DCJTB, and C545T was 100:5.81:0.342:0.304:0.394. It is observed that the blue dopant is the majority constituent among the dopant mixture. This may due to the fact that the excitons generated from the blue dopant can easily transfer their energy to other dopants. After the proper ratio is obtained empirically, the doped NPD can be prepared in large scale for mass production of white OLEDs.

A thin layer of poly(3,4-ethylenedioxythiophene)–poly(styrene) (PEDOT-PSS) film was spin-coated onto the UV ozone treated indiun-tin oxide (ITO) coated glass with a speed of 4000 rpm for 1 min and then baked at 115 °C for 50 min. A 30-nm-thick NPD and a 40 nm doped NPD (with the same ratio of NPD:DPVBi:rubrene:DCJTB:C545T as described previously; which is 100:5.81:0.342:0.304:0.394) layer were thermally evaporated successively on the PEDOT-PSS film for hole transporting and light-emitting layer, respectively. Following the evaporation of a 4-nm-thick BCP hole blocking layer and a 20 nm Alq_3 electron transporting layer, a bilayer consisting of 5 Å lithium fluoride (LiF) and 1000 Å of aluminum (Al) was evaporated to act as the cathode electrode. The fabrication process was carried out under a base pressure $\sim 3 \times 10^{-6}$ Torr and the deposition rates for organic materials, LiF, and Al were ~ 2, ~ 0.1, and ~ 7 Å/s, respectively. The effective emitting areas of the OLEDs were measured to be 12 mm^2.

Figure 3 shows the current–voltage ($I-V$) and brightness–voltage ($B-V$) characteristics of a white OLED. The maximum efficiency reaches ~ 2.5 cd/A and maximum brightness is 15 000 cd/m^2. Figure 4 shows the electroluminescent spectra from the same white OLED under different current densities ranging from 0.083 to 2.5 mA/mm^2. The spectra show several features correspond to the colors only in the visible range. It is observed that the features are well kept with different applied currents. For many multiplayer white OLEDs the Commission Internationale de I'Eclairage
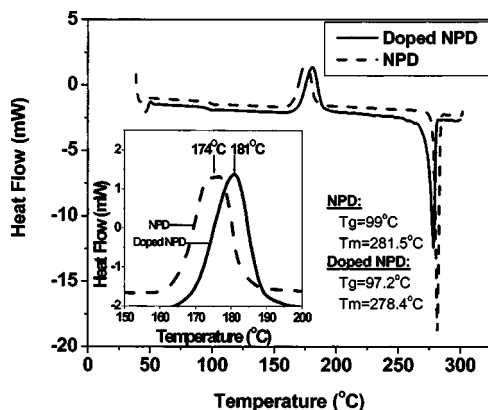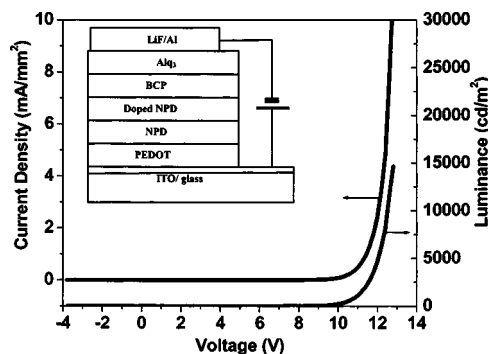

FIG. 2. Comparison of the DSC heating curves and thermal transition temperatures of the pure and doped NPD. (Heating rate is 5 °C/min and weight ratio for the doped NPD is NPD:DPVBi:C545T:Rubrene:DCJTB = 100:4.12:0.282:0.533:0.415.) (Inset is the enlarged crystallization transition peaks.)

FIG. 3. The current–voltage and luminescence–voltage characteristics of the white OLED with single color emitting doped NPD. (Inset is the device structure.)
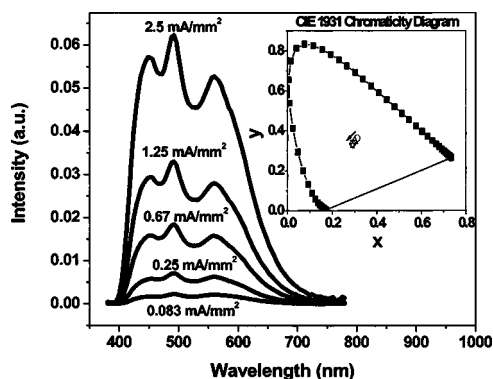
FIG. 4. The electroluminescent spectra from the white OLED at different current densities $(0.083-2.5 \text{ mA/mm}^2)$. The inset diagram shows the change of the CIE chromaticity diagram at different current densities $(0.083-2.5 \text{ mA/mm}^2)$ for the white OLED.

(CIE) coordinates often vary with applied current or voltage.[4] Our white OLED CIE coordinates vary only from (0.31, 0.36) to (0.29, 0.33) when the luminance increases from 1 (turn-on value) to 10 000 cd/m^2. In fact, the CIE coordinates almost focus exactly on (0.29, 0.33) when the luminance is above 500 cd/m^2. The inset diagram of Fig. 4 shows the change of CIE chromaticity diagram for the white OLED with different current densities $(0.083-2.5 \text{ mA/mm}^2)$. The chromaticity diagram in turn suggests that the white colors are quite stable with different device luminance.

In OLEDs, there are two common reasons responsible for the shift in device emission color with varying current/voltage. The first one is that the generation of high-energy excitons is easier under higher applied voltage, which may be attributed to the blueshift in emission. This kind of blueshift is very common in nearly all white OLEDs and even in some single color emission devices fabricated by co-evaporation of host and doping materials. The amount of the color shift can be practically reduced by changing the doping concentration. The second is the fact the recombination zone for electrons and holes in the devices can be relocated by the redistribution of electrical field due to applied voltage.[18] As stated before, many multiemission layer OLEDs have their emission from a combination of at least two different emission zones, these two zones must lie within in the vicinity of the charge recombination zone in order to give the two primary color emission. However, the corresponding film thickness and their interfacial properties can relocate the recombination zone, thus the emission colors from many white OLEDs are sensitive not only to the doping concentrations, applied voltage but also film thicknesses. Therefore, compared with single emission zone devices, it is more difficult to control and optimize all these parameters to yield stable device performance. To effectively anchor the recombination zone, the number of emission zones must first be reduced. In our white OLED structure, the recombination zone is confined essentially inside the doped NPD layer (only a part of it is in the vicinity of the BCP interface), the emission color is observed to be not sensitive to the thickness of the NPD layer.

The most important benefit of OLEDs with only one emission zone over the others is the fact that high emission color stability can be achieved. Based on the organic solid solution processing, the structure is greatly simplified since precise control of different evaporation sources at the same time has been avoided. Moreover, as the right weight ratios of the dopants have been obtained, the doped emitting materials can be prepared in large scale to realize the industrialization of OLEDs. It is worth noting that this is a general idea to fabricate OLEDs, it can be extended to fine-tone the color by adjusting the weight ratio for different dopants. In addition, other doping materials can also be incorporated in the system with no further complicating the fabrication process. This letter only demonstrates a typical doping system which includes some common doping materials.

In closing, a fabrication method of white OLEDs with one stable emission zone has been demonstrated. Stable full spectrum white light emission is obtained from the OLEDs with simplified device structure. The organic solid solution technique has proven to be an efficient tool for simplifying device fabrication and increasing device reproducibility. The development of this general idea for OLED fabrication is believed to be the next step toward the manufacturing of flat panel displays.

[1]C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **65**, 3610 (1987).
[2]C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989).
[3]L. S. Hung and C. H. Chen, Mater. Sci. Eng., R. **39**, 143 (2002).
[4]X. Y. Jiang, Z. L. Zhang, B. X. Zhang, W. Q. Zhu, and S. H. Xu, Synth. Met. **129**, 9 (2002).
[5]B. W. D'Andrade, M. E. Thompson, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **14**, 147 (2002).
[6]Y.-S. Huang, J.-H. Jou, W.-K. Weng, and J.-M. Liu, Appl. Phys. Lett. **80**, 2782 (2002).
[7]J. Kido, M. Kimura, and K. Nagai, Science **267**, 1332 (1995).
[8]J. Kido, W. Ikeda, M. Kimura, and K. Nagai, Jpn. J. Appl. Phys., Part 2 **35**, L394 (1996).
[9]K. O. Cheon and J. Shinar, Appl. Phys. Lett. **81**, 1738 (2002).
[10]S. S. Lee, T. J. Song, and S. M. Cho, Mater. Sci. Eng., B **95**, 24 #x0028;2002).
[11]C. H. Kim and J. Shinar, Appl. Phys. Lett. **80**, 2201 (2002).
[12]Y. S. Huang, J. H. Jou, W. K. Weng, and J. M. Liu, Appl. Phys. Lett. **80**, 2782 (2002).
[13]Z. Y. Xie, J. Feng, J. S. Huang, S. Y. Liu, Y. Wang, and J. C. Shen, Synth. Met. **108**, 81 (2000).
[14]Z. J. Chen, K. Ogino, S. Miyata, S. Miyata, Y. Lu, and T. Watanabe, J. Phys. D **35**, 742 (2002).
[15]C. W. Ko and Y. T. Tao, Appl. Phys. Lett. **79**, 4243 (2001).
[16]Y. Kawamura, S. Yanagida, and S. R. Forrest, J. Appl. Phys. **92**, 87 (2002).
[17]M. Grell, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, Adv. Mater. (Weinheim, Ger.) **9**, 798 (1997).
[18]E. Tutis, D. Berner, and L. Zuppiroli, J. Appl. Phys. **93**, 4594 (2003).