The Study of N-type Doping and Stamping Transfer Processes of Electron Transport Layer for Organic Light-emitting Diodes

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SUMMARY This paper presents 2-(hydroxyl) quinoline lithium (Liq) used as an n-type dopant to improve white hybrid organic light-emitting diode (WHOLEDs) performance. The Liq doped tris(8-hydroxyquinolinato) aluminum (Alq3) layer possessed enhanced electron injection, efficient hole and electron balance in the emitting layer, as one of the most essential issues for device applications. This work investigates the optimum recipe (Liq concentration and thickness) of Alq3:Liq n-type doped electron injection layer (EIL) for WHOLED devices by comparing the current density and efficiency results with conventional Alq3:LiF technique. A blocking layer or interlayer is inserted between emitting layer and EIL to avoid excitons quenched. In this work suitable material and optimum thickness of blocking layer for blocking layer are studied, too. Finally an optimal n-type doping recipe was employed to fabricate white hybrid organic light emitting diodes (WHOLED) to promote their power efficiency.

In addition, The solution-based small molecule organic light emitting diode (SM-OLED) manufacturing process is ideal for large scale, low-cost mass production. The solutions used in this process are typically high dissolvent materials. However, when used for fabricating multi-layered structures, the solutions can easily attack beneath layers and it becomes difficult to form a targeted layer. The enhanced SM-OLED performance is obtained through fabrication without solution intermixing problems using the stamping transfer method. The stamping process can fabricate high-performance SM-OLEDs based on solution-processes at low-cost. This stamping transfer technique utilizes a planar poly (dimethylsiloxane) (PDMS) elastomer. The PDMS stamps are suitable for a repeatable process since they are characterized by their low adhesion, durability and elasticity.

1. Introduction

Organic light-emitting devices (OLEDs) have been developed over many years emerging as one of the main contenders for the next generation flat information displays. However, the driving voltage of this device is still high and the conductive carrier concentration in organic materials is quite low [1]. Many studies have demonstrated that the interface between the electrode (anode and cathode) and organic layer plays a crucial role in OLED efficiency [2–4]. Using 2-(hydroxyl) quinoline lithium (Liq) as an organic electron transport material has been reported to facilitate electron injection from metal electrodes [5–7]. In the Alq3/LiF/Al fabrication process LiF thickness requires as thin as 0.5 nm. Such thin layer is very difficult to control run by run. So a suitable n-doping is an important technique for OLED industrial applications. The Liq doped Alq3 as n-doped system to carry out electron injection and transport was studied. This work investigates the optimum recipe (such as Liq concentration and thickness) of Alq3:Liq n-type doping electron injection layer (EIL) for OLED devices by comparing the current density and efficiency results with conventional Alq3:LiF technique. We dedicated to understand the electron injection and transport mechanisms in n-doping EIL. From the experiments and reference [8], it is found that excitons easily diffuse from EML to Alq3:Liq EIL and quench. So a blocking layer or interlayer is required to be inserted between EML and EIL to avoid excitons quenched. In this work suitable material and optimum thickness for blocking layer are studied, too. Finally an optimal n-type doping recipe was employed to fabricate white hybrid organic light emitting diodes (WHOLED) to promote their power efficiency.

2. Experiments

2.1 N-type Doping OLEDs Fabrication

ITO-coated glass substrates were immersed sequentially in an acetone and isopropyl alcohol ultrasonic bath for 15 min each, followed by a rinse in DI water. The substrates were blown dry with nitrogen gas and then treated with oxygen plasma for 1 min prior to use. The materials for use are WH112 as the hole injection layer, HTG-1 as the hole transport layer, UBH-15 as the blue host material, EPH-31 as the red host material, EB-502 as blue dopant and EPY-01 as yellow dopant. And two of the widely used materials for promoting electron transport are tris(8-hydroxyquinolinato) aluminum (Alq3) and tris(2,4,6-triMethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB). 3TPYMB is also employed as hole blocking layer for hole and interlayer between EML and EIL to avoid excitons quenched. All materials were purchased from e-Ray Optoelectronics Technology.

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The electron-only device fabricated in this work has the following configurations: ITO/Al (200 nm)/x (30 nm)/Al (150 nm), where x is Alq3 for device A, Alq3:Liq (10 wt%) for device B, Alq3:Liq (50 wt%) for device C, and Alq3:Liq (80 wt%) for device D, respectively. Liq was used as the dopant into Alq3 by co-deposition method. For the n-type layer in WHOLED, Alq3 and Liq were first mixed at different concentrations and solved in chlorobenzene solvent. After dried, it was put into vacuum chamber then evaporated. The WHOLED device structure is WHI112 (70 nm)/HTG1 (10 nm)/UBH15:EB502 (10 nm, 2 wt%)/EPH3:EPY01 (45 nm, 2 wt%)/y/Al (150 nm), where y is Alq3/Alq3:Liq with thickness of 0/30, 5/25, 10/20, and 15/15 nm, respectively. The WHOLED energy band diagrams are shown in Fig. 1 (a). All organic layers, doped layers and the cathode were deposited using thermal evaporation.

2.2 Stamping Transfer Processing OLEDs Fabrication

The first step is to pre-prepare the Poly(di-methylsilane) (PDMS) (silgard 184A). The PDMS is produced by mixing prepolymer and curing agent at the ratio of 10:1 by volume. After mixing, the solution was poured onto silicon wafer to achieve a plain surface stamp and then placed in vacuum to remove air bubbles. The solution was then poured onto silicon wafer to flatten its surface. After heating for an hour in an oven at 100°C, a PDMS plate is obtained. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as HIL was spin-coated onto an ITO glass substrate. For each experiment the spin-coating speed parameter was set up initially for 30 s. After spin-coating was completed the sample was immediately treated by baking on a hot plate at a temperature of 130°C for 10 min to remove the remaining solvent. The emitting layer, which consists of 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine(26DCzPPy) host material, blue dopant bis[2-(4,6-difluorophenyl) pyridinato-C2,N] (picolinate)iridium(III) (Flrpic) and red dopant tris[(4-n-hexyl-phenyl) quinoline] iridium (III) (Hex-Ir(phen)3), was mixed and dissolved in chlorobenzene and then spin-coated onto the PEDOT:PSS layer to form an EML and baked at 80°C for 15 min to improve the organic film properties.

The stamping is subsequently used to stamp the 1,3,5-tris (N-phenylbenzimidazol-2-yl) benzene (TPBi) as ETL onto the EML surface. PDMS was employed as a temporarily substrate. An intermediate UV ozone treatment is introduced to modify the PDMS surface so that solution-based TPBi film can be uniformly formed on top of the PDMS surface. A few drops of ETL solution were suspended in chlorobenzene and then applied to the PDMS stamp surface. The stamps were then spin-coated and then dried. The ETL coated PDMS stamp was then brought into contact with the EML coated substrate at 100°C. The PDMS stamp was then carefully peeled-off, leaving the ETL on the substrate. After releasing the layer, the sample was annealed at 120°C for 30 min on a hot plate. At the end of the device fabrication process LiF and Al were thermally evaporated as the cathode electrode. The resulting device structure is shown in Fig. 1 (b). The current-voltage-luminescence characteristics were measured with a Keithley 2400 source meter. EL spectra and CIE coordinates of the devices were analyzed via a spectrometer (PR650). All measurements were carried out under ambient conditions at room temperature.

3. Result and Discussions

3.1 N-type Doping for OLEDs

In the first study, electron only devices were fabricated by Alq3 doped with Liq in different concentrations. Three devices were fabricated in this work based on electron-only with the following configurations: ITO/Al (200 nm)/x (30 nm)/Al (150 nm), where x is Alq3, Alq3:Liq (10 wt%), Alq3:Liq (50 wt%) and Alq3:Liq (80 wt%), respectively. Figure 2(a) shows the current density versus voltage characteristics of the electron-only devices at room temperature. The current density of 20 mA/cm² was reached at 3.2 V, 2.9 V and 1.8 V for the pure Alq3, Alq3:Liq (10 wt%) and Alq3:Liq (50 wt%) device, respectively. This indicates substantial reduction in film resistance upon doping. Due to low binding energy between Li and hydroxyquinoline ligand [5], [13]. Liq dopants give rise to easy liberation of Li during cathode deposition in Liq system. The Liq doped Alq3 results in an electron transfer from Liq to Alq3[5], which increases the electron concentration in Alq3 films and moves...
the Fermi level close to the LUMO of Alq3 [14]. Higher doping concentrations (80 wt%), however, resulted in an increase in operating voltage to 3.0 V for 20 mA/cm² current density, which exceeds the injection limit for electrons due to too much Liq amount in Alq3 material. At higher doping concentration (80 wt%), Liq dopants become dominant in electron injection process from Al cathode. The injection barrier in highly doped Alq3:Liq/Al interface is higher than lowly doped Alq3:Liq/Al interface when disorder related barrier correction is applied to the interfaces [15].

The standard device using Alq3/LiF and n-doped device using Alq3:Liq (50 wt%) were compared in WHOLEDs. Figure 2(b) shows the current density versus voltage characteristics for these two device. It is clear that at the same operating voltage the Alq3/LiF device gives a higher current density than the Alq3:Liq device. If most of the flowing current is contributed by electron injection in Alq3/LiF device, electron and hole carrier amount will not be balanced. This results in a lower yield for Alq3/LiF device as shown in Fig. 2(b), where the yield is defined as luminance divided by current density. So standard device structure using Alq3/LiF may not be the optimal method for EIL, not only due to the difficulty of LiF thickness control run by run to deposit it as thin as 0.5 nm but also electron and hole carrier amount not balanced in the emitting layer. Alq3:Liqn-type layer thicknesses were produced to further investigate the enhanced electron-injection and transport mechanisms. The Liq doping concentration kept at 50 wt% in all WHOLED devices. An undoped interlayer, Alq3, was inserted between Liq doped Alq3 and EML. The undoped interlayer thickness was adjusted as Alq3/Liq (0/30 nm), Alq3/Alq3:Liq (5/25 nm), Alq3/Alq3:Liq (10/20 nm), and Alq3/Alq3:Liq (15/15 nm), respectively. Figure 3 shows the current efficiency versus current density characteristics of WHOLEDs with different Alq3/Liq/Liq thicknesses. A dramatic increase in the current efficiency was observed when Alq3 was inserted as an interlayer, especially in low current density region (0–15 mA/cm²). It can be seen that the current efficiency increases with increasing updoped Alq3 and decreasing Alq3:Liq thickness. In this way, we obtained the optimal thickness for Alq3/Liq/Liq layer, which is 10/20 nm. This device exhibited the highest luminance and current efficiency of 3760 cd/m² and 18.8 cd/A at 20 mA/cm², respectively. From the experiments and reference [8], it is found that excitons easily diffuse from EML to Alq3:Liq EIL and quench. So except for adjusting n-doping layer, a blocking layer or interlayer is required to be inserted between EML and EIL to avoid excitons quenched. 3TPYMB has higher electron mobility than Alq3 and high HOMO of 6.77 eV, as shown in Fig. 1(a), which can improve the electron injection and also block holes to be confined in the EML. So 3TPYMB was used as the interlayer and compared with Alq3 in WHOLEDs performance.

The WHOLED structure is WHI112/HTG1 (10 nm)/ UBH15:EB502 (10 nm, 2 wt%)/EPH3:EPY01 (45 nm, 2 wt%)/y/Al (150 nm), where y is Alq3/Alq3:Liq or 3TPYMB/Alq3:Liq. In the beginning, the hole injection layer WHI112 was kept at 70 nm and y used Alq3/Alq3:Liq or 3TPYMB/Alq3:Liq. In the beginning, the hole injection layer WHI112 was kept at 70 nm and y used Alq3/Alq3:Liq or 3TPYMB/Alq3:Liq (10/20 nm) and 3TPYMB/Alq3:Liq (10/20 nm), respectively, to compare the current density vs. voltage characteristics, as shown in Fig. 4(a). It is found that the WHOLED

![Fig. 2](image1.png)  
(a) Current density versus voltage characteristics in electron-only devices. (b) Current density versus voltage characteristics in WHOLEDs. The inset shows current density versus current efficiency characteristics of WHOLEDs.

![Fig. 3](image2.png)  
Current efficiency versus current density characteristics of WHOLEDs.
with WHI112 70 nm and 3TPYMB/Alq3:Liq 10/20 nm has lower current density than those with WHI112 70 nm and Alq3/Alq3:Liq 10/20 nm. It is due to the high HOMO of 3TPYMB which blocks holes and decreases the current density as the band diagram shown in Fig. 1(a). Therefore the corresponding power efficiency of WHOLED with WHI112 70 nm and 3TPYMB/Alq3:Liq 10/20 nm is lower than that of WHI112 70 nm and Alq3/Alq3:Liq 10/20 nm, as shown in Fig. 4(b).

Additionally, in order to further increase the hole current in WHOLED, the HIL thickness was optimized by decreasing the thickness from 70 to 55 nm and slightly increasing the n-doped layer thickness from 20 to 25 nm. When the HIL thickness was decreased from 70 to 55 nm the driving voltage decreased from 11.9 to 8.3 V and the current density increased apparently as shown in Fig. 4(a). Figure 4(b) shows the power efficiency versus current density characteristics of WHOLEDs with optimized hole injection and n-type doping layers. To further investigate the thickness of Alq3:Liq n-doped layer enhancement in charge injection and transport in WHOLEDs, the device based on the Alq3:Liq thickness of 25 nm was fabricated. The maximum current efficiency 23.2 cd/A was obtained in the device with HIL 55 nm and n-doped Alq3:Liq 25 nm (data not shown)

The power efficiency was increased from 4.5 to 7.4 lm/W at 20 mA/cm². The enhanced current efficiency is due to the improved charge balance as more electrons are injected from the Alq3:Liq n-type doping layer, transported through the 3TPYMB interlayer into the EML and 3TPYMB layer blocked holes in the EML, which improves the charge carrier balance and thus improves device efficiency. This indicates that decreased HIL and increased n-doped layer may provide as efficient hole and electron injection, thus enhancing the device efficiency by balancing the hole and electron currents.

3.2 Stamping Transfer Process for OLEDs

In the second study a solution-based fabrication method using a stamping transfer process is established to produce small molecule organic light emitting diodes (SM-OLEDs). The structure is ITO/PEDOS:PSS/26DCzPPy:Flrpic/TPBi/LiF/Al for blue SM-OLEDs, and a red HexIr(phq)3 was doped into 26DCzPPy:Flrpic layer for white SM-OLEDs. The PEDOS: PSS HIL and EML were fabricated via the spin-coating process. TPBi as ETL was fabricated using the stamping transfer process. The TPBi electron transport layer film was spin-coated onto the PDMS surface. The stamping transfer process was then used to transfer the PDMS onto the EML surface. Blue SM-OLEDs with different ETL stamping times were investigated. The TPBi stamping times of 80 s, 100 s, and 120 s were studied. Figure 5 shows the current efficiency versus current density characteristics of blue SM-OLEDs with different TPBi electron transport layer stamping times. As the results below 10 mA/cm², the current efficiencies of the devices are equal to zero. This could be due to the high operating voltage of these devices (6.2 V), which is supported lowering the luminance. Among these devices, the stamping time of 100 s device exhibited the best characteristics. It exhibits a luminance of 1240 cd/m², current efficiency of 2.48 cd/A and operating voltage of 6.2 V at 40 mA/cm².

Furthermore, device performance improvement of the due to a decrease in the ETL thickness from 32 to 27 nm is
observed, keeping the active layer thickness constant. The ETL thicknesses were prepared by varying the spin coating speed, using the same TPBi solution on PDMS. Figure 6(a) shows the current efficiency versus current density characteristics of white SM-OLEDs. We found that the white SM-OLED performance strongly depends on the ETL thickness. The device with 27 nm-thick ETL exhibited the best performance because electrons can inject efficiently into the EML. The luminance is 892 cd/m$^2$, while the current efficiency is 8.9 cd/A at 10 mA/cm$^2$. When the TPBi thickness was decreased from 32 to 27 nm the operating voltages decreased from 7.7 to 6.2 V. Judging from these results, ETL thickness based SMOLED is optimized at 27 nm thickness. The surface topography gets smoother as the film thickness is decreased to 27 nm. Interestingly, for the film thickness, thick film is spun at low speed and thin film is spun at high speed. These effects may be either direct, due to the change in the properties of the ETL itself, or indirect, due to the influence of the ETL surface properties on the stamping transfer properties. The CIE of TPBi thick 32 nm and 27 nm shifted from (0.36, 0.38) to (0.33, 0.37). The EL spectra of the white SM-OLEDs fabricated in different ETL stamping transfer thicknesses are shown in Fig. 6(b). The EL spectra were measured at 7 V. The solution emitting layer device showed a typical EL emission of Flrpic and Hex-Ir(phen)$_3$ based blue and yellow regions. However, the high intensity EL spectrum was observed from the device with an ETL thickness of 27 nm, higher than that obtained using 30 and 32 nm at the same operating voltage. This suggests that the charge transfer from the 27 nm thickness is more efficient. This indicates that the charge transfer from the cathode to EML occurs in the decreased ETL layers. The electron injection and transport ability could thus be enhanced more by incorporating less ETL thickness.

4. Conclusion

The introduction of Liq doped Alq$_3$ (10 nm) as n-doped layer and 3TPYMB (25 nm) as interlayer/hole blocking were effective in improving electron injection and hole blocking. The electron injection and transport efficiency were therefore both enhanced due to lower electron injection barrier and higher electron mobility, which improved the charge carrier balance in WHOLEDs, leading to higher device efficiency. The WHOLED efficiency increased from 18.1 to 22.3 cd/A at 20 mA/cm$^2$ when EIL changed from Alq$_3$/LiF to Alq$_3$:Liq. And an efficiency increases from 15.6 to 18.8 at 20 mA/cm$^2$ when Alq$_3$/Alq$_3$:Liq thickness changed from 0/30 to 10/20 nm. Furthermore, the WHOLED efficiency increases from 18.8 to 23.2 at 20 mA/cm$^2$ when HIL thickness decreased from 70 to 55 nm, and 3TPYMB was used as interlayer between EML and EIL. It is proposed that Liq doped Alq$_3$ can be used as an efficient electron injection layer for WHOLEDs. And using solution-based processing and ETL stamping transfer employed as an alternative method for white SM-OLED. The blue SM-OLED efficiency was increased from 1.02 to 2.48 cd/A at 50 mA/cm$^2$ when stamping time was changed from 80 to 100 s. In addition, the white SM-OLED efficiency increases from 8.25 to 8.9 cd/A at 10 mA/cm$^2$ and The CIE were shifted from (0.36, 0.38) to (0.33, 0.37) when the ETL stamping thickness decreased from 32 to 27 nm. As a result, efficient multilayered SM-OLEDs have been developed by stamping transfer, which allows for the replacement of the thermal evaporation needed for the deposition of the organic layers for future display devices.

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References


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