Low driving voltage and high stability organic light-emitting diodes with rhenium oxide-doped hole transporting layer

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The authors report a promising metal oxide-doped hole transporting layer (HTL) of rhenium oxide (ReO_3)-doped N,N'-diphenyl-N,N'-bis (1,1′-biphenyl)-4,4′-diamine (NPB). The tris(8-hydroxyquinoline) aluminum-based organic light-emitting diodes with ReO_3-doped NPB HTL exhibit driving voltage of 5.2–5.4 V and power efficiency of 2.2–2.3 lm/W at 20 mA/cm^2, which is significantly improved compared to those (7.1 V and 2.0 lm/W, respectively) obtained from the devices with undoped NPB. Furthermore, the device with ReO_3-doped NPB layer reveals the prolonged lifetime than that with undoped NPB. Details of ReO_3 doping effects are described based on the UV-Vis absorption spectra and characteristics of hole-only devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2754635]

Reduction of driving voltage of organic light-emitting diodes (OLEDs) is an important issue to improve the power efficiency in flat panel displays and solid-state lighting applications.[1] One of the most powerful solutions to reduce the driving voltage is to use doping concept in the electron and/or hole transporting layer.[1–9] To date, several doping systems based on the organic dopants have been developed.[1–6] However, their material instability remains to be further enhanced.[6,7] To overcome the problem, metal oxide-based doping materials such as tungsten oxides (WO_3), molybdenum oxides (MoO_3), and vanadium oxides (V_2O_5) have been introduced recently for hole transporting layer (HTL) or hole injection layer and attracted much attention due to their better material stability.[7–9] However, their material toxicity and high evaporation temperatures are still problematic for use in conventional OLED processing,[8] which requires further development of other oxide-based doping systems.

In general, doping in HTL occurs through the charge transfer from the highest occupied molecular orbital (HOMO) of the host material to the lowest unoccupied molecular orbital of the dopant material.[3] If considering the effective doping of common hole transporting materials having HOMO of 5.0–5.5 eV, thermally stable metal oxide dopants with high work function (or electron affinity) of about 5.5 eV are preferentially required. In this study, we used transparent rhenium oxides (ReO_3) as a dopant material in HTL. The material has high work function of about 6.0 eV (Ref. 10) so that charge transfer complex is easily formed as proved by absorption spectra. The hole-only device with ReO_3-doped N,N'-diphenyl-N,N'-bis (1,1′-biphenyl)-4,4′-diamine (NPB) produces Ohmic-like current density–voltage characteristics with electrical conductivity of 7.5×10^{-6} S/cm. Furthermore, low melting points (160–300 °C) of rhenium oxides,[11] which is relatively low among other metal oxides, facilitate codeposition with organic molecules by conventional thermal evaporator.[8]

150 nm thick indium tin oxide (ITO) coated glass substrates were prepared and cleaned with acetone and isopropyl alcohol. Before depositing organic layers by thermal evaporator, the surface of ITO was treated with UV ozone for 10 min. To fabricate the OLEDs, 60 nm thick HTL, 15 nm thick undoped NPB layer, and 60 nm thick tris(8-hydroxyquinoline) aluminum (Alq_3) emission layers were sequentially deposited on the ITO coated glass, followed by deposition of LiF/Al cathode. For the HTL, 0–25 wt % rhenium oxides (ReO_3) (Aldrich) were doped in NPB layer. The active area of the devices was 2×2 mm^2. Hole-only devices consisting of ITO/HTL/Al structures were also fabricated. The current density–voltage-luminance (J-V-L) characteristics of the devices were measured by a Keithley 2400 semiconductor parameter analyzer and Photo Research PR-650 spectrophotometer. All devices were encapsulated prior to the measurement. The absorption spectra of HTL were measured by means of UV-Vis spectrophotometer (Cary 5000).

Figure 1 shows the UV-Vis absorption spectra of the

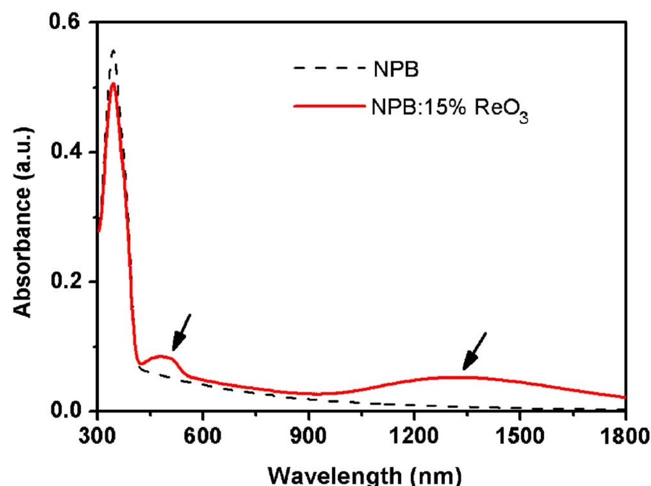

FIG. 1. (Color online) UV-Vis absorption spectra of undoped NPB (60 nm) and NPB:15% ReO_3 (60 nm) films deposited on quartz substrate.

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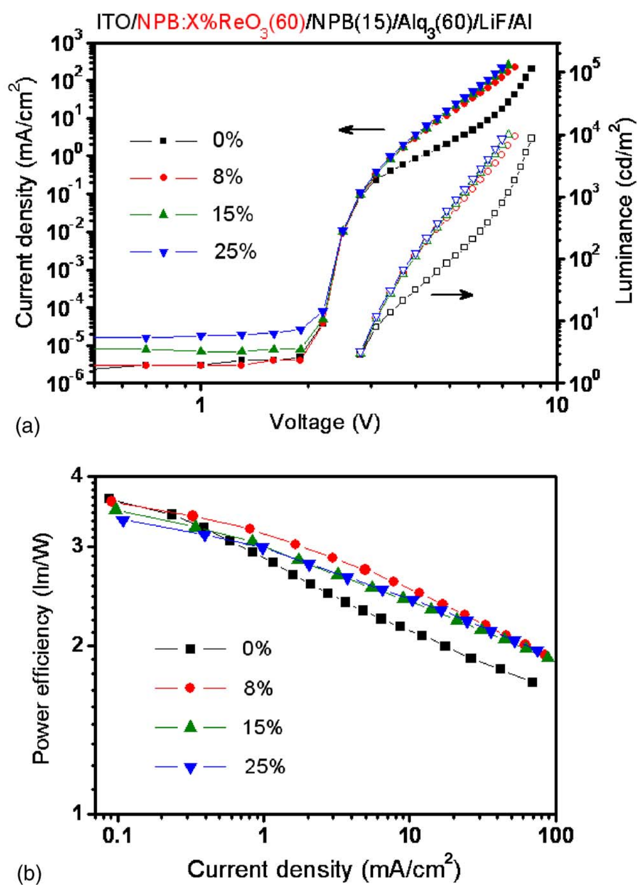

FIG. 2. (Color online) (a) Current density–voltage–luminance characteristics and (b) power efficiency–current density of the OLEDs with NPB:X% ReO_3 (60 nm)/NPB (15 nm)/Alq_3 (60 nm)/LiF (1 nm)/Al (100 nm).

undoped NPB (60 nm) and NPB:15% ReO_3 (60 nm) films on quartz. The absorption spectrum of the NPB film shows only strong absorption peaks at the wavelength less than 400 nm, while the ReO_3-doped NPB film reveals additional absorption peaks at around 500 and 1350 nm wavelengths (as indicated by the arrows), which indicates the formation of charge transfer complex.[2,7,8]

Figure 2(a) shows *J-V-L* characteristics of the OLEDs consisting of NPB:X% ReO_3/NPB/Alq_3/LiF/Al structures. The device with undoped NPB layer exhibits operation voltage of 7.1 V at 20 mA/cm^2. In contrast, the devices with ReO_3-doped NPB layer show significantly reduced operation voltages. For example, the devices with 8%, 15%, and 25% ReO_3-doped NPB layers show the operation voltages of 5.4, 5.2, and 5.2 V at 20 mA/cm^2, respectively. These results indicate that doping of ReO_3 in the NPB layer effectively enhances the hole injection and transport. The power efficiency–current density characteristics of the OLEDs with ReO_3-doped NPB and undoped NPB layers are also shown in Fig. 2(b). Whole devices with ReO_3-doped NPB layers show improved power efficiency (2.2–2.3 lm/W at 20 mA/cm^2) compared to that (2.0 lm/W) with undoped NPB layer, which is attributed to the lowering of operation voltage. It is noteworthy, however, that doping of ReO_3 in the NPB layer causes somewhat decreased external quantum efficiency of the devices (not shown), which is mainly caused by the enhanced hole injection and consequent charge imbalance.[7]

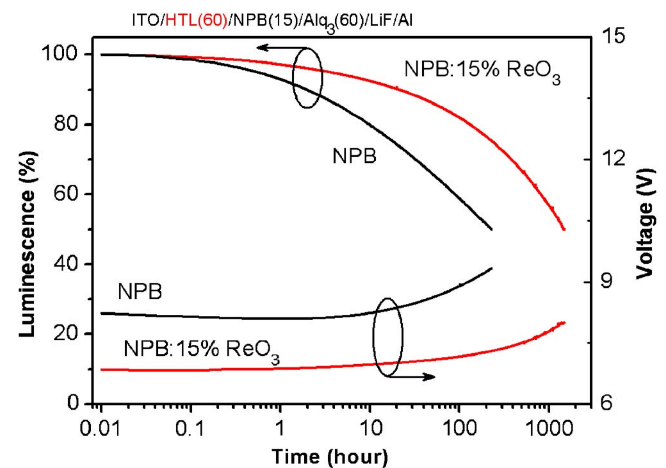

FIG. 3. (Color online) Lifetime of the OLEDs consisting of NPB:X% ReO_3/NPB/Alq_3/LiF/Al structures measured at 2000 cd/m^2.

Figure 3 shows the lifetime of devices with NPB:X% ReO_3/NPB/Alq_3/LiF/Al structures. The device with undoped NPB layer shows a half-lifetime of only 227 h at the initial luminance of 2000 cd/m^2, whereas that with 15% ReO_3-doped NPB layer exhibits a half-lifetime of 1470 h. This suggests that doping of ReO_3 in the NPB layer improves the long-term stability of OLEDs.

To understand hole injection and transport characteristics of the ReO_3-doped NPB layer, hole-only devices with ITO/HTL/Al structures were fabricated. In this device geometry, electron injection from the Al cathode to the HTL is prohibited due to the large injection barrier. Figure 4 shows *J-V* characteristics of the hole-only devices consisting of NPB:15% ReO_3 (60 nm), NPB:15% ReO_3 (60 nm)/NPB (15 nm), and undoped NPB (75 nm) layers. It is shown that the *J-V* characteristic of the device with undoped NPB layer follows general trapped charge limited current (below 1.5 V) and space charge limited current (above 1.5 V) models.[12] In contrast, it is clearly shown that the hole-only device with NPB:15% ReO_3 layer exhibits Ohmic-like *J-V* characteristic. The electrical conductivity was calculated to be 7.5×10^{-6} S/cm. This behavior strongly indicates that doping of ReO_3 in NPB layer enhances the charge injection and trans-

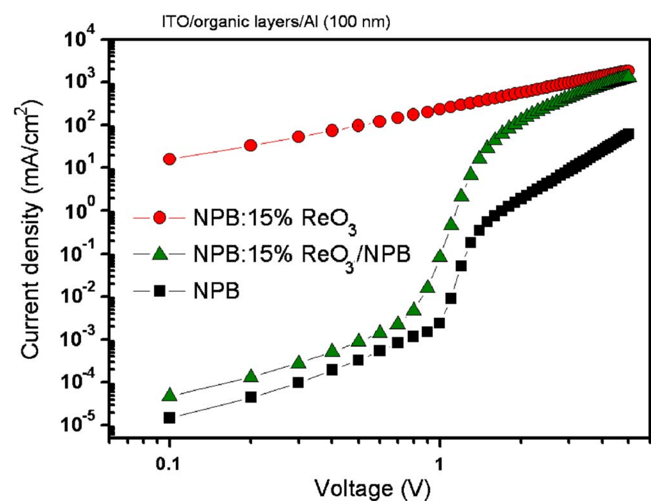

FIG. 4. (Color online) The current density–voltage characteristics of the hole-only devices with NPB:15% ReO_3 (60 nm), NPB:15% ReO_3 (60 nm)/NPB (15 nm), and undoped NPB HTL (75 nm).

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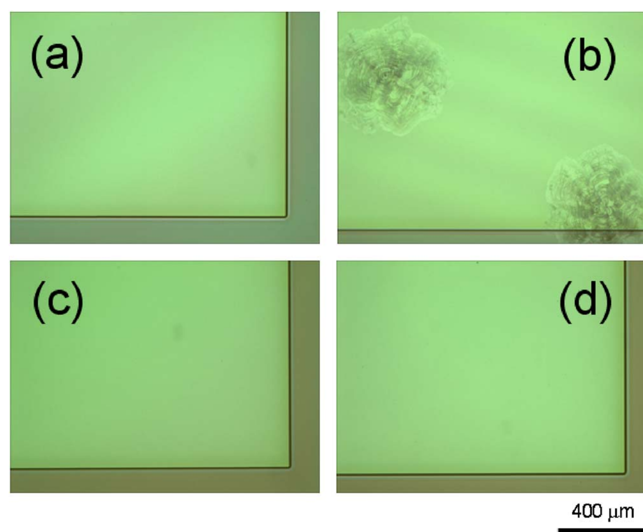

FIG. 5. (Color online) Optical micrographs of the undoped NPB (75 nm) samples: (a) before and (b) after annealing at 140 °C; and of NPB:15% ReO_3 (60 nm)/NPB (15 nm) samples: (c) before and (d) after annealing at 140 °C.

port at the anode/organic interface due to the increase of the free hole concentration in HTL via charge transfer reactions (Fig. 1).[3,5] However, it is noted that although the hole-only device with NPB:15% ReO_3 layer shows Ohmic behavior, the hole-only device with NPB:15% ReO_3/NPB layers, namely, real HTL structure in OLEDs, follows similar behavior with *J-V* characteristic of the undoped NPB layer. This suggests that, for the device with NPB:15% ReO_3/NPB layers, the current conduction is largely limited by the undoped NPB layer. Thus, in order to further reduce operation voltage of the devices, decrease of the undoped NPB layer thickness is desirable. However, for the OLEDs, it may also cause other problems such as exciton quenching[4] and excess hole injection and transport into the emission layer,[2] resulting in further decrease of the quantum efficiency. Still, the current level in the device with NPB:15% ReO_3/NPB layer shows one order of magnitude higher current density at the same voltage to contribute to lowering the driving voltage, as shown in Fig. 2.

Figure 5 displays the optical micrographs of undoped NPB (75 nm) and 15% ReO_3-doped NPB (60 nm)/NPB (15 nm) layers before and after annealing at 140 °C for 90 min in nitrogen ambient. For the undoped NPB layer [Figs. 5(a) and 5(b)], the surface morphology of NPB layer is severely damaged by thermal annealing, which results in the creation of crystallized NPB regions (about 400 μm diameter), as shown in Fig. 5(b). It is noted that the crystallized NPB regions begin to be formed at 130 °C, exhibiting crystallized regions of 80–100 μm diameter (not shown). The 15% ReO_3-doped NPB layer, however, shows no significant morphological change even after annealing at 140 °C [Fig. 5(d)]. This result clearly implies that doping of ReO_3 in NPB layer is very effective in suppressing the formation of crystallized NPB regions, which results in the significant improvement of the device stability,[13,14] as shown in Fig. 3. In particular, it is believed that doping-induced charge transfer complex (Fig. 1) strengthens the morphology of the NPB layer and thus enhances the long-term stability of the OLEDs.[14] Detailed mechanisms about doping-induced enhancement of device stability are under further investigation.

In summary, we investigated a promising ReO_3-doped NPB HTL system for high performance OLEDs. It was shown that doping of ReO_3 caused formation of charge transfer complex, indicating possible creation of free holes in HTL. The Alq_3-based OLEDs with ReO_3-doped NPB layer exhibited much reduced driving voltages of 5.2–5.4 V and power efficiency of 2.2–2.3 lm/W at 20 mA/cm^2 due to the enhancement of hole injection and transport. It was also shown that the OLEDs with ReO_3-doped NPB layer showed significantly improved device stability, which is mainly attributed to the stabilization of the NPB film morphology.

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