

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

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Keywords : OLED, rhenium oxide, doping

Abstract

We demonstrate fluorescent green organic light-emitting diodes employing a rhenium oxide (ReO_3)-doped *N,N'*-diphenyl-*N,N'*-bis(1,1'-biphenyl)-4,4'-diamine (NPB) hole transporting layer (HTL). The devices exhibit significantly reduced driving voltages as well as prolonged lifetime. Details of ReO_3 doping effects are described in terms of charge transfer complex and stabilization of HTL morphology.

1. Introduction

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 [1-7]. To date, several doping systems based on the organic dopants have been developed [1-3]. However, their material instability remains to be further enhanced [4]. 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) and attracted much attention due to their better material stability [4-7]. However, their material toxicity and high evaporation temperatures are still problematic for use in conventional OLED processing [5, 7], 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 (LUMO) of the dopant material [2]. 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 [8] so that charge transfer complex is easily formed as proved by absorption spectra. Furthermore, low melting points (160–300 °C) of rhenium oxides [9], which is relatively low among other metal oxides, facilitate co-deposition with organic molecules by conventional thermal evaporator.

2. Experimental

150 nm-thick-indium tin oxide (ITO) coated glass substrates were prepared and cleaned with acetone and isopropyl alcohol. Prior to the deposition of 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 un-doped 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 $2 \times 2 \text{ mm}^2$. 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).

3. Results and discussion

Figure 1 shows the UV-Vis absorption spectra of un-doped NPB (60 nm) and ReO₃-doped NPB (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 ReO₃-doped NPB films reveal additional absorption peaks at around 500 and 1350 nm wavelengths, which indicates the formation of charge transfer complex [5].

Figure 2(a) shows *J-V-L* characteristics of the OLEDs consisting of NPB:X% ReO₃/NPB/Alq₃/LiF/Al structures. The device with un-doped NPB layer exhibits driving voltage of 7.1 V at 20 mA/cm². In contrast, the devices with ReO₃-doped NPB layer show significantly reduced driving voltages. For example, the devices with 8, 15, and 25% ReO₃-doped NPB layers show the driving voltages of 5.4, 5.2, and 5.2 V at 20 mA/cm², respectively. These results indicate that doping of ReO₃ in the NPB layer effectively enhances the hole injection and transport. The power efficiency-current density characteristics of the OLEDs with ReO₃-doped NPB and un-doped NPB layers are also shown in Fig. 2(b). Whole devices with ReO₃-doped NPB layers show improved power efficiency (2.2–2.3 lm/W at 20 mA/cm²) compared to that (2.0 lm/W) with un-doped NPB layer, which is attributed to the lowering of driving voltage. It is noteworthy, however, that doping of ReO₃ in 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 [4].

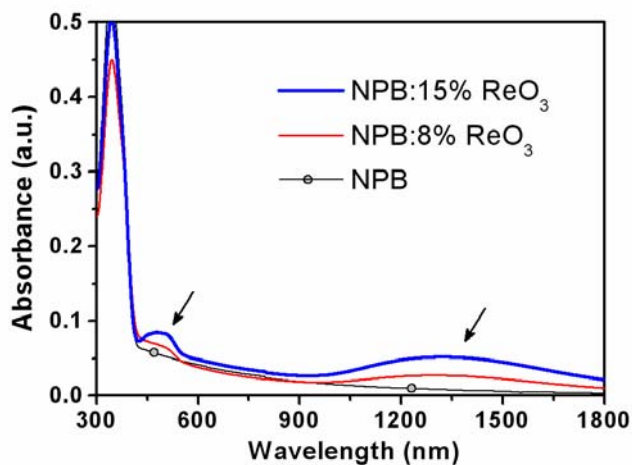


Fig. 1. UV-Vis absorption spectra of un-doped NPB and ReO₃-doped NPB films.

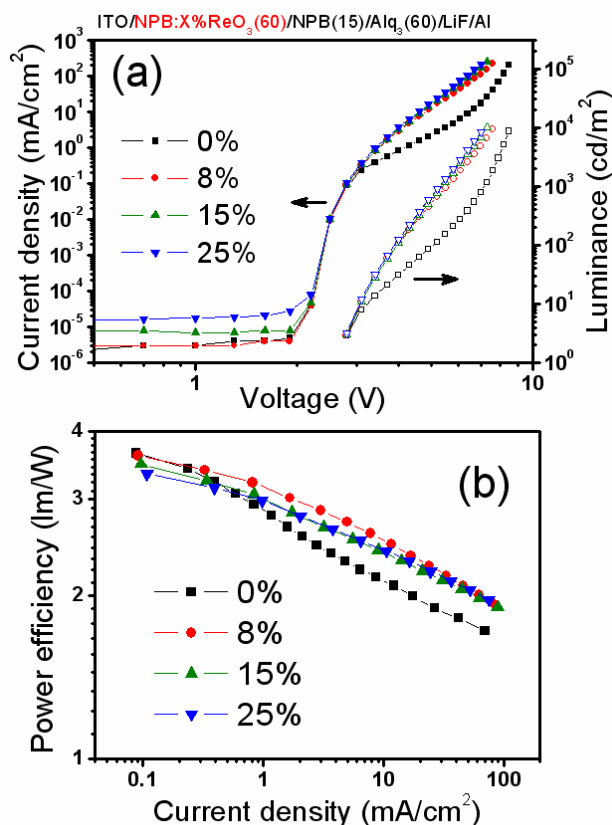


Fig. 2. (a) The current density-voltage-luminance characteristics and (b) power efficiency-current density of the OLEDs.

Figure 3 shows the lifetime of devices with NPB:X% ReO₃/NPB/Alq₃/LiF/Al structures. The device with un-doped NPB layer shows a half-lifetime of only 227 h at the initial luminance of 2,000 cd/m², whereas that with 15% ReO₃-doped NPB layer exhibits a half-lifetime of 1,470 h. This suggests that doping of ReO₃ in the NPB layer improves the long-term stability of OLEDs.

Figure 4 displays the optical micrographs of un-doped NPB and 15% ReO₃-doped NPB/NPB layers before and after annealing at 130–140 °C for 90 min in nitrogen ambient. For the un-doped NPB layer, the crystallized NPB regions begin to be formed at 130 °C, exhibiting crystallized regions of 80–100 μm diameter (Fig. 4(b)). It is noted that the surface morphology of NPB layer is further severely damaged by increased annealing temperature, which results in the crystallized NPB regions of about 400 μm diameter as shown in Fig. 4(c). However, the 15% ReO₃-doped NPB layer shows no significant morphological change even after thermal annealing (Fig. 4(e) and (f)).

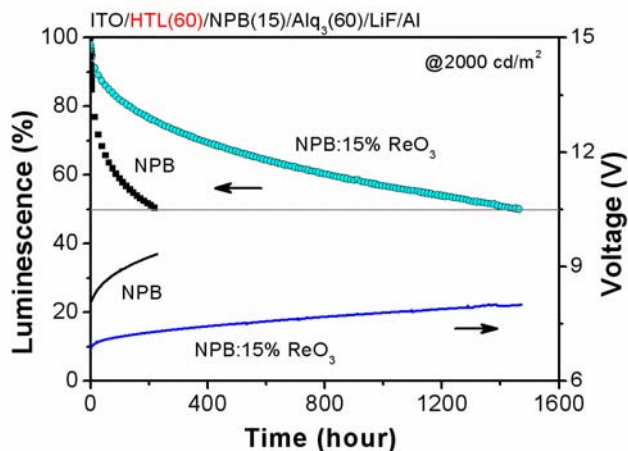


Fig. 3. The lifetime of the OLEDs.

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 [10] 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 [10].

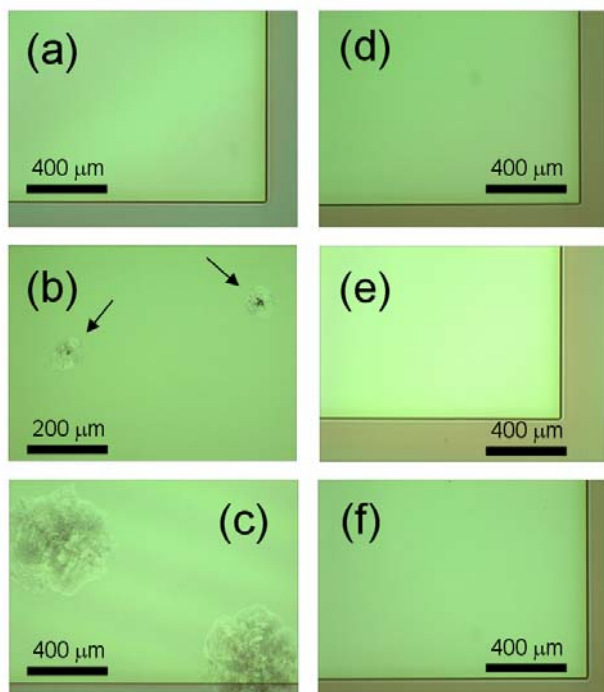


Fig. 4. Optical micrographs of un-doped NPB (75 nm) samples: (a) before, (b) after 130 °C, and (c) after 140 °C annealing; and of NPB:15% ReO_3 (60 nm)/NPB (15 nm) samples: (d) before, (e) after 130 °C, and (f) after 140 °C annealing.

To further improve the performance of OLEDs with ReO_3 -doped NPB HTL, the device structure was modified by replacing Alq_3 electron transporting layer (ETL) with bis(10-hydroxybenzo(h)quinolate) beryllium (BeBq_2). Figures 5(a) and (b) show J - V - L and power efficiency-current density characteristics of the modified OLEDs, respectively. The OLED with BeBq_2 ETL exhibits further reduced driving voltage of 4.7 V and improved power efficiency of 2.6 lm/W at 20 mA/cm^2 , compared to those (5.4 V and 2.3 lm/W, respectively) from the device with Alq_3 ETL. This achievement is mainly attributed to the enhancement of electron injection or transporting property [4, 11].

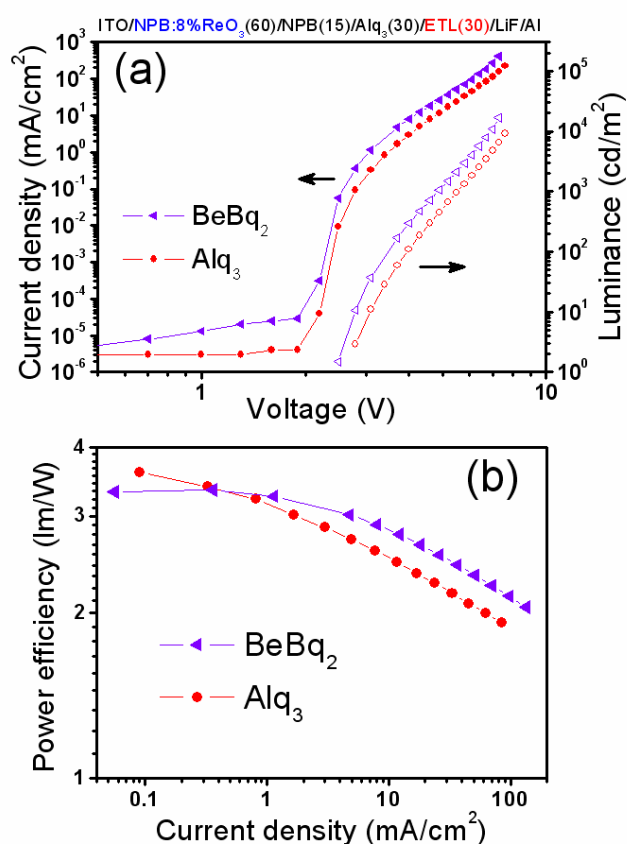


Fig. 5. (a) The current density-voltage-luminance characteristics and (b) power efficiency-current density of the OLEDs.

4. Conclusion

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

8–25% ReO₃-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/cm² due to the enhancement of hole injection and transport. It was also shown that the OLEDs with ReO₃-doped NPB layer showed significantly improved device stability, which is mainly attributed to the stabilization of the HTL film morphology. By using BeBq₂ ETL, the OLEDs with ReO₃-doped NPB HTL produced further reduced driving voltage of 4.7 V and enhanced power efficiency of 2.6 lm/W at 20 mA/cm².

5. Acknowledgments

The authors thank the Ministry of Commerce, Industry, and Energy, Samsung SDI and Dongwoo Finechem. Co. for their financial support of this work.

6. References

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