

Low-Driving-Voltage, Long-Lifetime Organic Light-Emitting Diodes with Molybdenum-Oxide (MoO_3)-Doped Hole Transport Layers

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We report low-operating-voltage, long-lifetime organic light-emitting diodes (OLEDs) with a molybdenum-oxide (MoO_3)-doped N,N' -di(1-naphthyl)- N,N' -diphenylbenzidine (α -NPD) layer between the indium tin oxide and the α -NPD. The current density-voltage-luminance characteristics and the lifetime were studied for various MoO_3 doping concentrations and thicknesses. The devices with α -NPD layers of various MoO_3 doping concentrations and thicknesses exhibited lower driving voltage and higher power efficiency compared with the undoped devices. Furthermore, the device with MoO_3 -doped hole transport layer showed a longer lifetime and a much reduced operational voltage variation. The optical absorption spectra of the MoO_3 -doped α -NPD layer showed two new peaks, around 500 and 1400 nm, indicating that charge transfer complexes had formed between MoO_3 and α -NPD. The p-type doping of α -NPD by MoO_3 improved hole injection. In addition, AFM images show that the morphology of the MoO_3 -doped α -NPD layer improved with increasing MoO_3 doping concentration. Therefore, the improved device performance can be attributed to the higher hole-injection efficiency and the improved morphology of the MoO_3 -doped α -NPD layer.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) have emerged as a new flat-panel display technology with superior display qualities since the first demonstration of efficient light emission by Tang and Vanslyke [1]. Intensive research has been carried out to improve the device performances, such as luminous efficiency, driving voltage and lifetime. Since the operating voltage and the efficiency of organic light-emitting diodes (OLEDs) rely on the injection and the recombination of charge carriers, it is very important to enhance the charge injection efficiency [2, 3]. However, the work function difference between the electrode and the organic materials results in a potential energy barrier, limiting the carrier injection at organic/electrode interfaces [4]. One way to improve the carrier injection is the insertion of an appropriate carrier injection layer, which leads to an effectively lower potential barrier [5–9]. At the interface of the transparent indium tin oxide (ITO) layer and the hole-transport layer (HTL), vari-

ous materials, such as copper phthalocyanine (CuPC) [5], copper hexadecafluorophthalocyanine (F_{16}CuPC) [6], 4,4',4''-tris{N, (3-methylphenyl)-N-phenylamino} - triphenylamine) (m-MTDATA) [7], poly(ethylene-dioxy thiophene):poly(styrene sulfonic acid) (PEDOT:PSS) [8] and conducting fluorocarbon coatings (CF_x) [9] have been inserted as a hole-injection layer (HIL).

Nowadays, p-doped HTLs with various oxidative dopants, such as FeCl_3 [10], SbCl_5 [11] and $\text{F}_4\text{-TCNQ}$ [12], have been reported to lower the operating voltage and transition metal oxides have emerged as a new candidate for a hole injection and transport material in OLEDs and organic photovoltaic cells [13, 14]. In this letter, we report low-operation-voltage, long-lifetime OLEDs with hole transport layers of various MoO_3 doping concentrations and thicknesses.

II. EXPERIMENT

We fabricated the OLEDs with a N,N' -di(1-naphthyl)- N,N' -diphenylbenzidine (α -NPD) hole transport layer, a *tris*(8-hydroxyquinoline) aluminum (Alq_3) electron transport layer and a LiF/Al cathode. The substrate was

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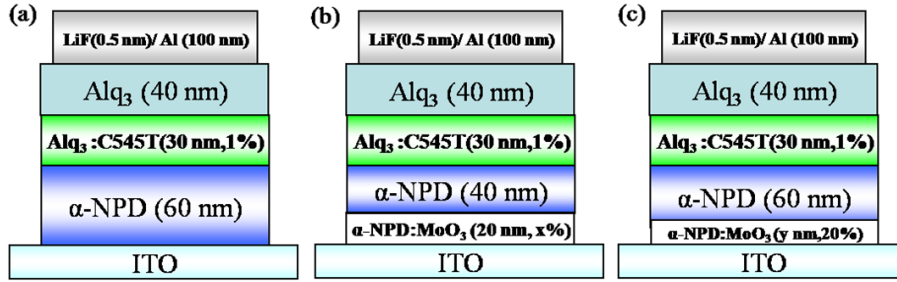


Fig. 1. Structures of (a) a reference device, (b) devices with MoO₃-doped α -NPD layers of various doping concentrations (2 ~ 100 %) and (c) devices with various thicknesses (5 ~ 20 nm) of the MoO₃-doped α -NPD layer.

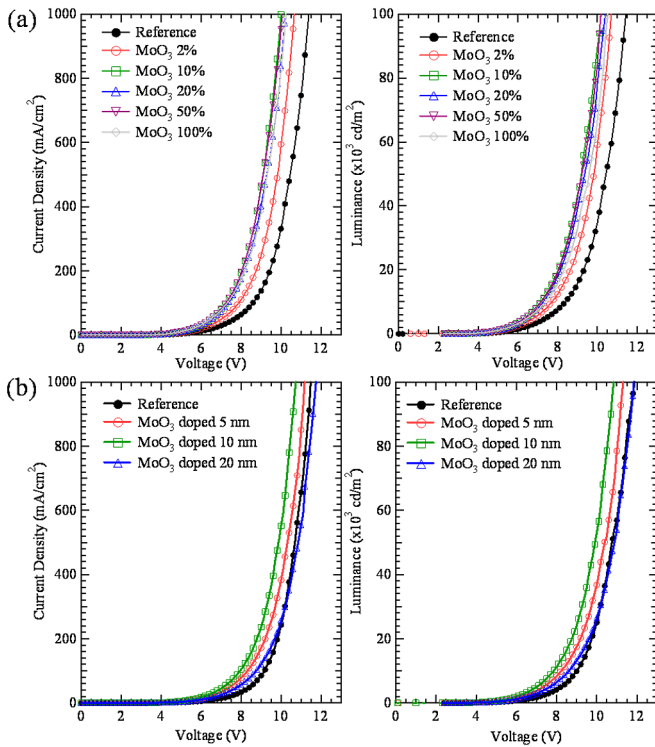


Fig. 2. Current density-voltage and luminance-voltage characteristics: (a) devices with various doping ratios (2 ~ 100 %) of the MoO₃-doped α -NPD layer and (b) devices with various thicknesses (5 ~ 20 nm) of the MoO₃-doped α -NPD layer.

a pre-patterned ITO glass. It was cleaned by ultrasonication in isopropyl alcohol, acetone and methanol for 10 minutes, respectively and rinsed in de-ionized (DI) water for 5 minutes between several cleaning steps. Then, the ITO substrate was dried in an oven kept at 120 °C for more than 30 minutes. After cleaning and drying, the ITO substrate was treated with ultraviolet ozone (UVO) for 4 minutes in order to improve the device performance [15]. Then, the organic layers and the cathode were deposited under a high vacuum ($<3 \times 10^{-6}$ Torr) without breaking vacuum. The active area of the OLED, defined by the overlap of the ITO and the Al cathode, was 1.96

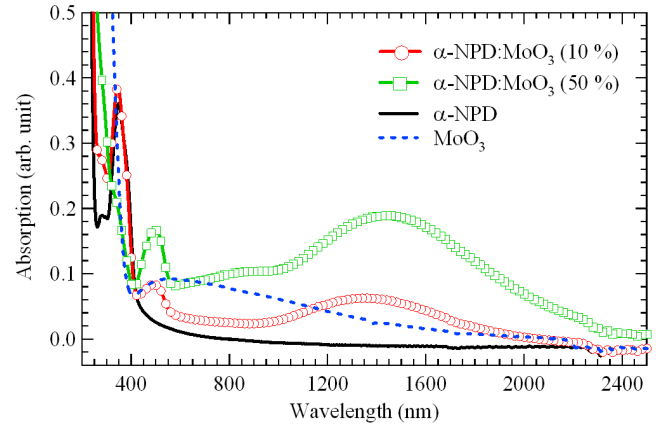


Fig. 3. Optical absorption spectra for 10 % (circles) and 50 % MoO₃-doped α -NPD (squares), undoped α -NPD (solid line) and MoO₃ films (dotted line) deposited on quartz substrates.

mm². The deposition rates for the organic layers and the metal were 0.1 ~ 0.2 nm/sec and 0.3 ~ 0.4 nm/sec, respectively.

The current-voltage-luminance (I-V-L) characteristics were measured with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a photomultiplier tube (PMT) through an ARC 275 monochromator. The external quantum efficiency (QE) of the electroluminescence (EL) was calculated from the EL intensity measured by using a the calibrated Si photodiode placed at a normal angle to the device surface, assuming the device to be a Lambertian source.

III. RESULT AND DISCUSSION

Figure 1 shows the structure of (a) a reference device, (b) devices with MoO₃-doped α -NPD layer of various doping concentrations (2 ~ 100 %) and (c) devices with various thicknesses (5 ~ 20 nm) of the MoO₃-doped α -NPD layer. The hole transport layer (α -NPD, 60 nm), the emitting layer (10-(2-benzothiazolyl)-2,3,6,7-tetramethyl-1H, 5H, 11H-(1)-benzopyrroprano (6,7-8-

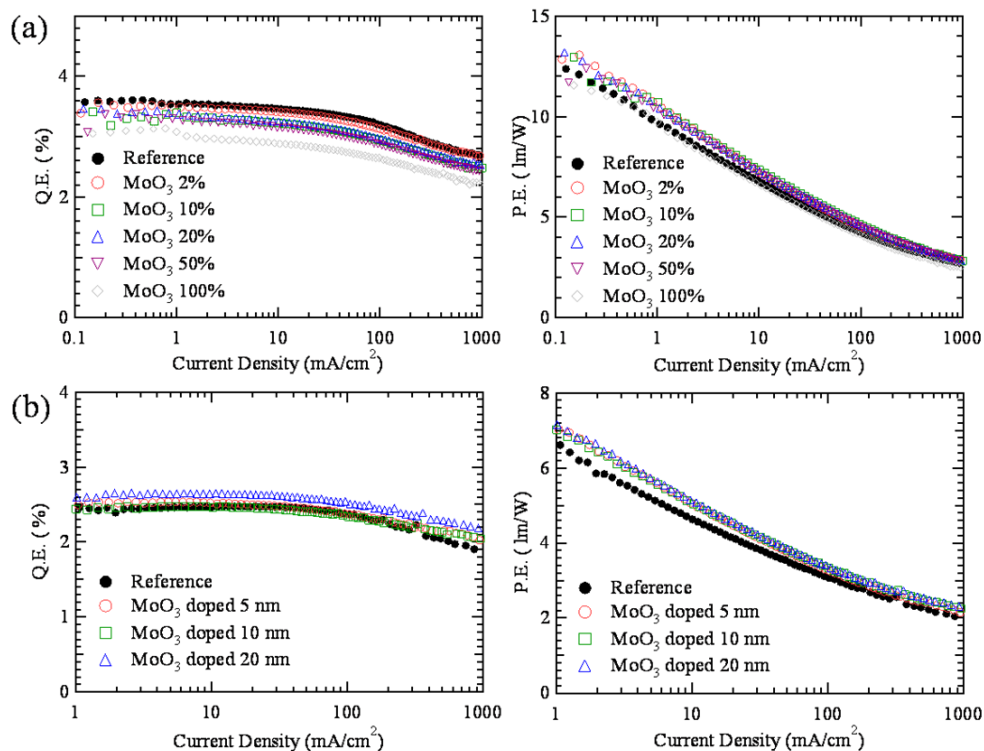


Fig. 4. Power efficiency (P.E.) and external quantum efficiency (Q.E.) as functions of current density: (a) devices with various doping ratios (2 ~ 100 %) of the MoO₃-doped α -NPD layer and (b) devices with various thicknesses (5 ~ 20 nm) of the MoO₃-doped α -NPD layer.

i,j)quinolizin-11-one (C545T)-doped Alq₃, 30 nm, 1 %), the electron transport layer (*tris*(8-hydroxyquinoline) aluminum; Alq₃, 40 nm) and the LiF (0.5 nm)/aluminum (100 nm) cathode were thermally evaporated sequentially without breaking vacuum.

Figure 2 shows the current density-voltage (J-V) and the luminance-voltage (L-V) characteristics for (a) devices with MoO₃ doping ratios from 2 % to 100 % and (b) devices with various thicknesses of the MoO₃-doped α -NPD layer from 5 nm to 20 nm. Compared to the device with an undoped α -NPD in Figure 2 (a), even a small MoO₃ doping obviously decreases the driving voltage significantly and the current increases with increasing MoO₃ doping concentration. In addition, Figure 2 (b) shows that the operating voltage decreases and the current increases as the thickness of MoO₃-doped α -NPD layer increases up to 10 nm. The results indicate that the MoO₃-doped α -NPD layer reduces the potential barrier for hole injection at the ITO interface.

In order to investigate the mechanism of the enhanced hole injection caused by inserting the MoO₃-doped α -NPD layer, we measured the optical absorption spectra for 10 % and 50 % MoO₃-doped α -NPD, undoped α -NPD and MoO₃ films deposited on quartz substrates. Figure 3 clearly shows two new peaks, one at about 500 nm and the other around 1400 nm. Both peaks are absent in the absorption spectra of both pure α -NPD and MoO₃ films and increase with increasing MoO₃ concentration.

Similar absorption spectra with two peaks, around 500 and 1400 nm, were observed for the FeCl₃-doped α -NPD films [16]. Therefore, these peaks can be assigned to a charge transfer complex between MoO₃ (or FeCl₃) and α -NPD, resulting in p-type doping of α -NPD (α -NPD cations) [16]. Due to the p-type doping of α -NPD by MoO₃ or FeCl₃, the Fermi level shifts and the width of the space charge layer decreases with increasing doping concentration, resulting in an improved hole injection [17].

Although the MoO₃-doped α -NPD layer at the ITO interface facilitates the hole injection, increasing its thickness by more than about 10 nm leads to an increased operating voltage and a decreased current, as shown in Figure 2. This behavior can be understood since the additional MoO₃-doped α -NPD layer increases the overall resistance of the device.

Figure 4 shows the power efficiency (P.E.) and the external quantum efficiency (Q.E.) as functions of the current density for the devices shown in Figure 2. Compared with the reference device of the undoped α -NPD layer, the device with the MoO₃-doped α -NPD layer exhibited a somewhat higher power efficiency. For the device with the MoO₃-doped α -NPD layer, the higher hole injection efficiency leads to a slight unbalance of electrons and holes, thus resulting in slightly lower Q.E. However, the insertion of the MoO₃-doped α -NPD layer reduced the operational voltage significantly and thereby resulting in

Table 1. Device performance of devices with various doping ratios (2 ~ 100 %) and thicknesses (5 ~ 20 nm) of the MoO₃-doped α-NPD layer.

At a luminance of 1000 cd/m ²				
Thickness of Doping Layer (nm)	Current Density (mA/cm ²)	Voltage (V)	Q.E. (%)	P.E. (lm/W)
0	8.2	6.4	2.4	4.8
5	8.8	5.6	2.5	5.2
10	9.25	5.4	2.5	5.2
20	9.0	5.9	2.6	5.2
Doping Ratio (%)	Current Density (mA/cm ²)	Voltage (V)	Q.E. (%)	P.E. (lm/W)
0	8.6	5.7	3.4	6.9
2	8.5	5.2	3.4	7.5
10	8.8	4.9	3.2	7.5
20	8.9	5.0	3.2	7.4
50	9.8	5.0	3.1	7.1
100	10.5	5.0	2.9	6.5

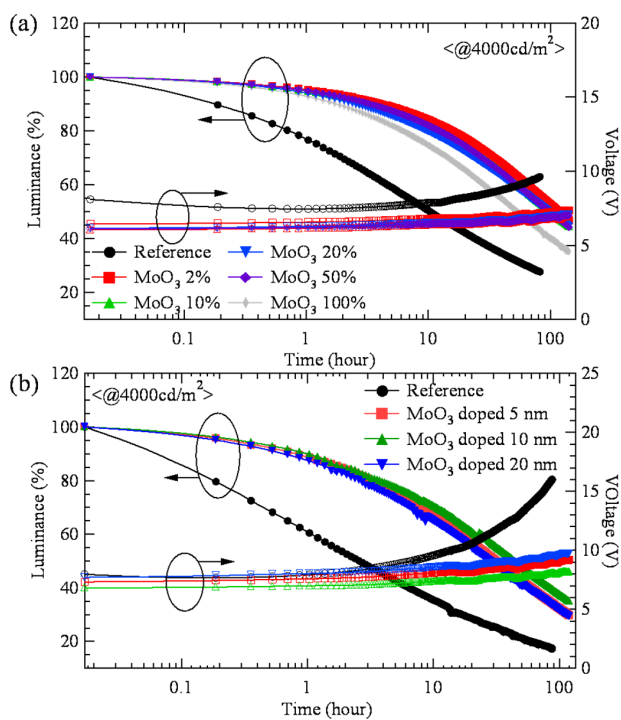


Fig. 5. Operational stability for devices with various doping ratios (2 ~ 100 %) (a) and thicknesses (5 ~ 20 nm) of the MoO₃-doped α-NPD layer (b) driven at constant current levels with an initial luminance of 4000 cd/m² at room temperature.

a much enhanced luminous power efficiency. The performances of all the devices are summarized in Table 1.

Figure 5 shows the operational stability for devices with various doping ratios (2 ~ 100 %) and thicknesses (5 ~ 20 nm) of the MoO₃-doped α-NPD layer. The measurements were carried out at room temperature by ap-

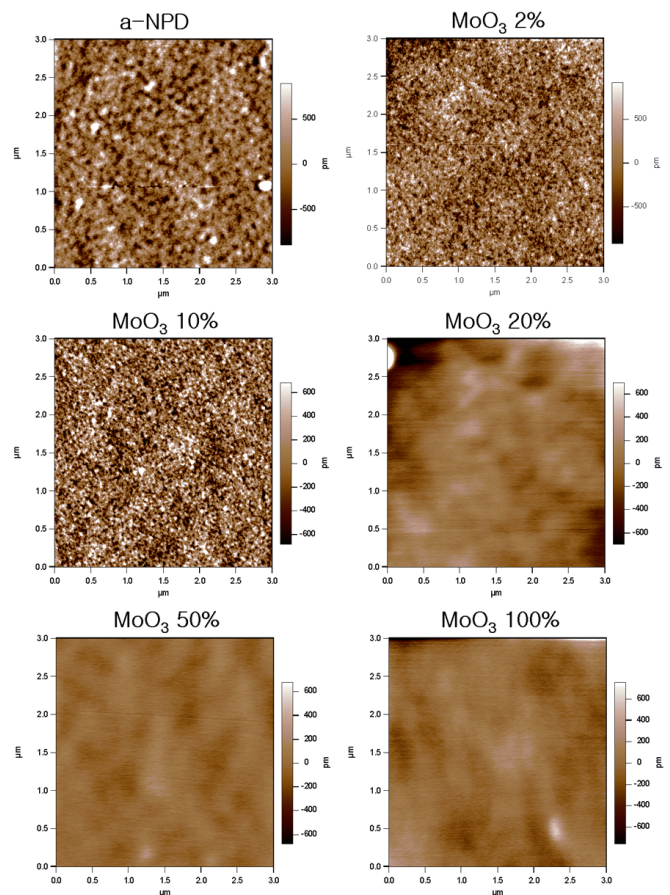


Fig. 6. AFM images of the MoO₃-doped α-NPD layers. Note that the surface roughness decreases with increasing MoO₃ doping concentration the α-NPD layer.

plying a constant current for an initial luminance of 4000 cd/m² to each device. The devices with the MoO₃-doped

α -NPD layer show much longer operational lifetimes and much reduced variations in the operational voltage. The enhanced hole injection and the improved surface morphology of the interface between the electrode and the MoO₃-doped α -NPD layer most likely enhance the device's lifetime and stability. Figure 6 shows atomic force microscopy (AFM) images of the MoO₃-doped α -NPD layers. Clearly, the surface roughness decreases with increasing MoO₃ doping concentration the α -NPD layer.

IV. CONCLUSION

We have demonstrated the insertion of a MoO₃-doped α -NPD layer at the interface between ITO and α -NPD reduces the driving voltage and increases the power efficiency. In addition, the device with the MoO₃-doped α -NPD layer shows a longer lifetime and a much reduced operational voltage variation. By measuring the device characteristics for various doping ratio and thicknesses of the MoO₃-doped α -NPD layer, we find that an optimum doping ratios and thickness are about 20 % and 10 nm, respectively. New absorption peaks, around 500 and 1400 nm, in the optical absorption spectra of the MoO₃-doped α -NPD layer indicate that charge transfer complexes form between MoO₃ and -NPD, resulting in a p-type doping of α -NPD. In addition, AFM images show that the morphology of the MoO₃-doped α -NPD layer improves with increasing MoO₃ doping concentration. Therefore, the higher hole-injection efficiency and the improved morphology of the MoO₃-doped α -NPD layer between the ITO and the α -NPD lead to the improved device performance.

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