Electrical Properties of the Molybdenum oxide doped Hole transport layer

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Abstract

We report on a highly conductive and stable hole transporting layer comprising of N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) doped with molybdenum oxide (MoO_3). Compared to the reference device, the device with MoO_3-doped hole transporting material exhibits higher conductivity and thermal stability. The temperature dependence of the current-voltage characteristics are studied for various MoO_3 doping concentration.

1. Introduction

The operating voltage and efficiency of organic light-emitting diodes (OLEDs) rely on the injection and recombination of charge carriers, it is very important to enhance the charge injection efficiency [1, 2]. However, the work function difference between the electrode and organic materials results in a potential energy barrier, limiting the carrier injection at organic/electrode interfaces [3]. One way to improve the carrier injection is the insertion of an appropriate carrier injection layer which leads to effectively lower potential barrier. At the interface of the transparent indium tin oxide (ITO) and the hole-transport layer (HTL), various materials such as copper phthalocyanine (CuPC) [4], or 4,4', 4"-tris{N, (3-methylphenyl)-N-phenylamino} -triphenylamine) (m-MTDATA) [5], poly(ethylene-dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) [6], and conducting fluorocarbon coatings (CF_x) [7] are inserted as a hole-injection layer (HIL).

In addition, p-doped HTLs with various oxidative dopants such as $FeCl_3$ [8], $SbCl_5$ [9] and F_4-TCNQ [10] have been reported to lower the operating voltage. Recently, Ikeda *et al.* reported that molybdenum oxide (MoO_3) forms a charge-transfer complex with N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) and the operating voltage of OLEDs can be reduced by using the MoO_3-doped α–NPD layer as a HIL [11]. However, the electrical characteristics of the inorganic-oxide doped HTL is not well understood. Therefore, in this work, we studied in detail the temperature dependence of the current-voltage characteristics of the MoO_3-doped α–NPD films with various MoO_3 concentrations in the range of 0-20 % in order to understand the conduction mechanism in the MoO_3-doped α–NPD films.

2. Results

We have fabricated hole-only devices to investigate the hole conduction properties of the MoO_3 doped α-NPD layer as the MoO3 doping concentration varies in the range of 0-20 %. The substrate is a pre-patterned indium-tin-oxide (ITO). 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. And 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. Then the organic layers and cathode were all deposited under the high vacuum ($< 3 \times 10^{-6}$ Torr) without breaking vacuum. The active area of the devices, defined by the overlap of the ITO and the AL cathode, was 1.96 mm^2. The deposition rates for the organic layers were 0.1~0.2 nm/sec and 0.3~0.4 nm/sec for metal. The current-voltage (I-V) characteristics were measured with a Keithley 236 source-measure unit. Figure 1 shows the device structures. Fig. 1 (a) is the reference device where the hole transport layer (α–NPD, 100 nm), and aluminum (100 nm) cathode is thermally evaporated sequentially without breaking the vacuum. Fig. 1 (b) shows the device structure with the MoO_3-

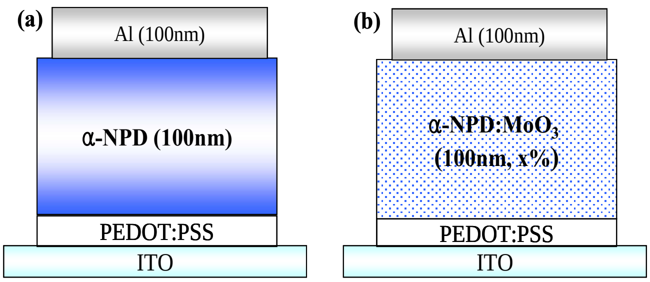

Figure 1. The device structure of reference (a), and MoO_3 doped α-NPD device (b) , (x%=2,5,10,20%)

doped α –NPD (the thickness=100 nm).

Fig. 2 shows the current density-voltage (J-V) characteristics of the MoO_3 doped α − NPD device compared to the reference device. The MoO_3 doped α − NPD device exhibits symmetric J-V characteristics with several orders of magnitude higher current-density under both forward and reverse bias, compared to the undoped α − NPD device. The current increases with the MoO_3 doping concentration and, therefore, the conductivity can be controlled by the doping ratio. The result indicates that doping MoO_3 into the hole transporting layer effectively reduces the hole injection barrier and forms an ohmic contact.

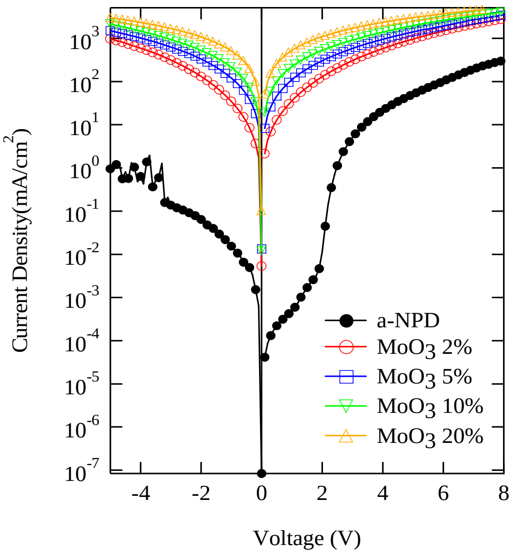

Figure 2. The current density-voltage characteristic

Fig. 3 shows the temperature dependence of the current-density at a forward bias of 5 V in an Arrhenius plot. The MoO_3-doped α − NPD devices show very stable I-V characteristics up to 400 K while the undoped devices show unstable I-V characteristics above about 330 K. Therefore, the MoO_3-doped α − NPD film has high thermal stability. The devices with MoO_3-doped α − NPD films exhibit a thermally-activated temperature dependence at high temperature (T>100 K) and a very weak temperature dependence below about 100 K. Thus, the conduction mechanism in the MoO_3 doped α − NPD can be described as a multiple trapping conduction at high T>100 K and tunneling through the trap at T<100 K. The activation energy E_a was calculated by fitting the data at T>100 K to the Arrhenius equation

$$J \propto e^{-E_a / k_B T} \qquad (1)$$

E_a decreases as the MoO_3 doping concentration increases. Therefore, the MoO_3-doped α - NPD

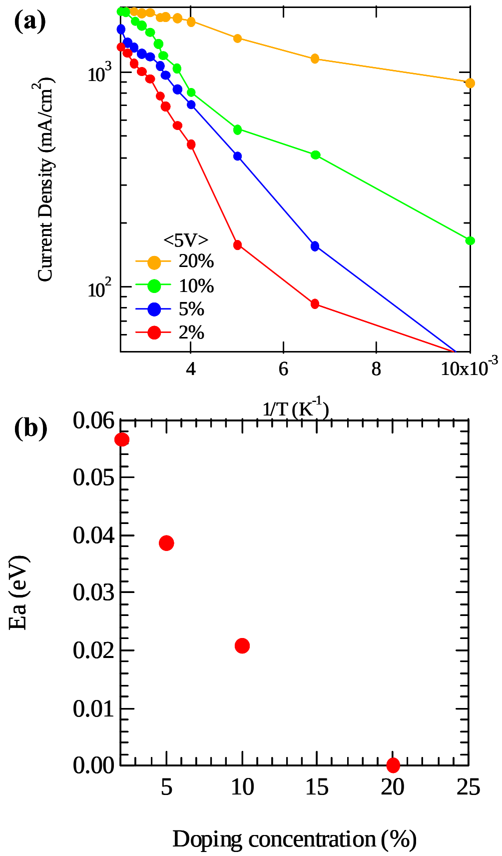

Figure 3. (a) Current-density vs. 1/T characteristics at 5V (b) activation energy vs. doping concentration

films with high MoO_3 doping concentration are an excellent hole injection layer with high electrical conductivity.

3. Summary

We studied the electrical conduction mechanism of the MoO_3-doped α- NPD films. The MoO_3 acts as a p-type dopant in α- NPD. Doping MoO_3 into a hole transport material increases carrier concentration and lowers the thermal activation energy for multiple trapping transport of holes. Therefore, MoO_3-doped HTLs can significantly reduce the operating voltage and enhance the stability of OLEDs.

4. Acknowledgements

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5. References

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