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Improved Hole-injection Contact by Employing an Ultra-thin MoO_3 Carrier Injection Layer

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Abstract: An efficient hole-injection contact was achieved for organic light-emitting diodes (OLEDs) based on molybdenum oxide (MoO_3) as the buffer layer on indium tin oxide. The significant effect of MoO_3 is that the devices show low operational voltage and high electroluminescence efficiency in a wide range of MoO_3 thickness. The device with a 1 nm-thick MoO_3 layer shows the best performance, the current efficiency is enhanced by 1.6 times by comparing with the control device. Capacitance-voltage measurement demonstrated that hole injection is enhanced in low operational voltage through the addition of MoO_3 . Results of the hole-only devices revealed that ohmic hole injection is formed at ITO/ MoO_3 /NPB interface. Photovoltaic measurements confirmed that the improved hole injection is due to the reduction of barrier height, which is resulted from the addition of transition metal oxide.

Key words: OLED; molybdenum oxide; capacitance measurements; ohmic injection; photovoltaic measurements

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1 Introduction

Organic light-emitting diodes (OLEDs) have been developed because of their potentials in cheap, lightweight, mechanically flexible, large display and light source applications^[1~4]. The fundamental process in organic electroluminescent devices involves the injection of hole and electron from the electrode into the emissive material in order to form neutral bound excited states (excitons) that can recombine through photon emission. Numbers of experimental results have demonstrated that the degradation of OLEDs is directly related to the anode interface stability^[5,6]. One of the most used methods is to introduce a buffer layer on the indium tin oxide (ITO) to solve this problem, such as Al_2O_3 ^[7], WO_3 ^[8], CuO_x ^[9], V_2O_5 ^[10], Pr_2O_3 ^[11] and NiO ^[12], etc. Although efforts have been made in various

studies to improve electroluminescence efficiency by introducing a p-type metal oxide into the hole transport layer, a thorough understanding of the mechanisms still waits to be attained.

Pervious reports revealed that MoO_3 is a wide-gap material with a band gap of ~ 3.1 eV and a superb hole-injection material for ITO ($\Phi_{\text{ITO}} = 4.8$ eV). MoO_3 can be conveniently deposited by thermal evaporation and the evaporated MoO_3 forms a transparent and homogeneous film, making it rather compatible with the OLED fabrication^[13,14]. Seki *et al.*^[15] reported that a large downward energy shift (1.0 eV) obtained by UV photoemission spectroscopy is observed at Alq_3/Al interface due to the interfacial dipole, dramatically reducing the electron injection barrier from Al cathode to Alq_3 electron transport layer. Nevertheless, a large hole injection barrier generally exists between ITO and the hole

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transport layer N-N-diphenyl-N-N-bis(1-naphthyl)-1,1-biphenyl-4,4-diamine (NPB), forming the imbalance of the barrier height of hole and electron injection. In this paper, we study the role of the insertion of an ultra-thin MoO₃ between hole transport layer and ITO in OLEDs. The efficient hole-injecting and electron-blocking (electron affinity = 2.3 eV) by MoO₃ layer leads to significant enhancement in device performance and efficiency. Capacitance-voltage measurements demonstrated that the hole injection is enhanced in low operational voltage through the addition of MoO₃. Results of the hole-only devices revealed that ohmic hole injection is formed at ITO/MoO₃/NPB interface. Photovoltaic measurements confirm that the improved hole injection is due to the reduction of barrier height resulted from the addition of transition metal oxide.

2 Experiments

OLEDs with the device structures of ITO/MoO₃ (0, 0.5, 1, 3, 20 nm)/NPB(40 nm)/tris(8-hydroxyquinoline) aluminum (Alq₃)(60 nm)/Al(100 nm) were prepared by conventional thermal deposition in a vacuum chamber with a base pressure of 4×10^{-4} Pa. LiF was not used as electron injection layer because of the low electron barrier between Alq₃ and Al reported by Seki *et al*^[15]. ITO-coated glasses used have a film thickness of 18 nm and sheet resistance of about 40 Ω/□. The active emission area of the devices is 0.36 cm². The devices with the structure of ITO/MoO₃(0, 1 nm)/NPB(80 nm)/MoO₃(5 nm)/Al(100 nm) were prepared for reference. The deposition rates for the organic materials, MoO₃ and Al layer is 0.1 nm/s, 0.01 nm/s and 0.20 nm/s, respectively. All materials are commercial grade and used without further purification. Current density-voltage-luminance-current efficiency (*J-V-L-η*) characteristics were measured by using a Keithley source measurement unit with a calibrated silicon photodiode. The capacitance-voltage (*C-V*) spectroscopy was made using an impedance analyzer (HP4192A) under the condition of 1 kHz frequency and the condition of oscillating voltage of 0.5 V during the direct current bias voltage scan-

ning. The photovoltaic measurements were carried out under an illumination intensity of 100 mW/cm² (AM 1.5G).

3 Results and Discussion

3.1 Device Performances

The *J-V* characteristics of ITO/MoO₃(0, 0.5, 1, 3, 20 nm)/NPB/Alq₃/Al devices were measured with various thickness of MoO₃ buffer layer inserted between ITO and NPB, as shown in Fig. 1(a). The current initially increases with the increase of MoO₃ thickness, and significantly reaches a maximum value at 1 nm MoO₃ thickness, then decreases with the increasing of MoO₃ thickness. For the case of the device with the MoO₃ buffer layer, the injection of hole

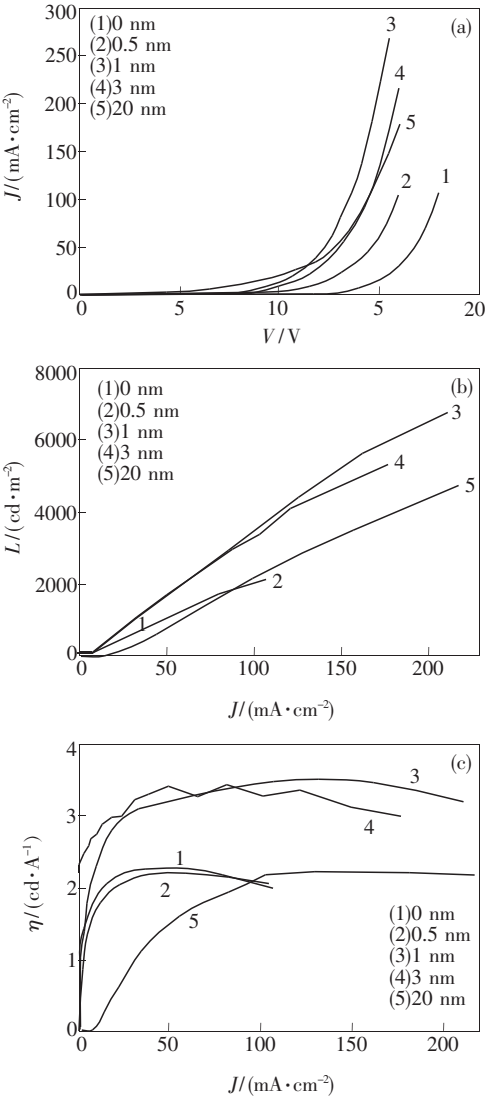


Fig. 1 (a) *J-V*, (b) *L-J* and (c) η -*J* characteristics for the devices with different MoO₃ thickness.

from ITO into the hole transport layer becomes more effective. The L - J and η - J characteristics of the devices are presented in Fig. 1 (b) and Fig 1 (c). Compared to the ITO control device (2.2 cd/A and a luminance of 941 cd/m²), the device with the thickness of 1 nm MoO₃ layer provides the highest current efficiency of 3.5 cd/A and a luminance of 4 413 cd/m². The current efficiency improvement as much as 1.6 times is achieved. Even for the 20 nm thick MoO₃ device, the current efficiency of 2.3 cd/A and a luminance of 2 909 cd/m² are reached at a current density of 130 mA/cm². Such effect can be explained by the enhancement of the hole injection and the electron block by MoO₃.

3.2 Injection Mechanism

3.2.1 Capacitance-voltage performance

Fig.2 shows the C - V curves of the ITO/MoO₃ (0, 1 nm)/NPB/Alq₃/Al devices under forward bias voltage. All devices exhibit more capacitance increase with bias voltage. It can be seen that the inflexion of maximal hole injection for the 1 nm MoO₃ device begins at 10 V, much lower than the ITO control device which begins at 19 V. The capacitance increase after the inflexion indicates the injection of hole majority carriers. However, the capacitance increase for device without MoO₃ between 10 V and 13 V indicates the injection of electron majority carriers, then it decreases for the hole carriers begin to inject from the anode. These results clearly illuminate that the ultra-thin MoO₃ layer can substantially improve the hole injection from the ITO anode.

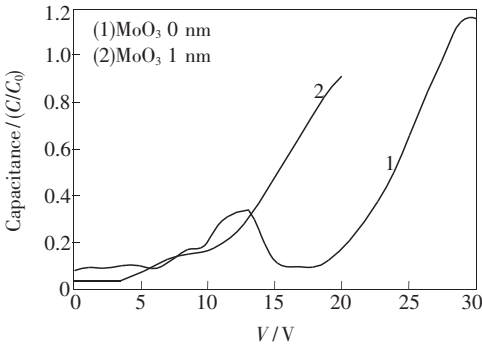


Fig. 2 C - V characteristics for ITO/MoO₃ (0, 1 nm)/NPB/Alq₃/Al devices

3.2.2 Hole-only device performance

To examine the efficient hole-injection characteristics at the ITO/MoO₃/NPB interfaces, we prepared two hole-only devices. As shown in Fig. 3, the J - V characteristics are plotted. It is observed that the ITO/ MoO₃ anode (1 nm)/NPB (80 nm)/ MoO₃ (5 nm)/Al device has the higher current density, whereas the ITO anode/NPB (80 nm)/ MoO₃ (5 nm)/Al device displays the lower current density. It is found that the current density is proportional to the square of the voltage ($J \propto V^2$) for the MoO₃ anode device, which means that ohmic hole injection can be achieved at the ITO/MoO₃/NPB interfaces and the J - V characteristic of this device is controlled by a space-charge-limited current (SCLC) theory^[16]. In the case of the ITO anode device, the J - V characteristic is well controlled by a trap-charge-limited current (TCLC) theory, whose equation is given by

$$J \propto K (V^{m+1}/d^{2m+1}), \tag{1}$$

where K is a constant in relation to the material, $m = E_t/kT$ (k is Boltzman constant, T is the device operating temperature, and E_t is the distance of trap isolated from the energy level of conduction band). Fitting the J - V characteristic provides that m is equal to 2.5. The higher slope for the ITO anode device is associated with the deeper trap energy below the quasi-Fermi level E_n in the band gap of the organic layer. The improvement in the J - V characteristics with the introduction of the MoO₃ layer suggests the formation of efficient hole injection at the ITO/MoO₃/

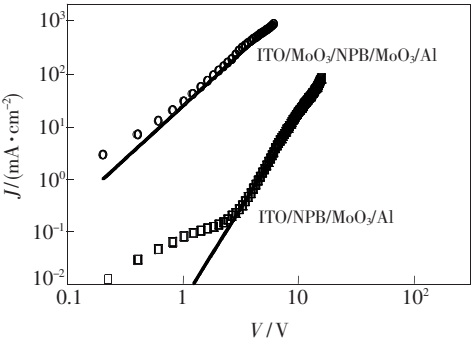


Fig. 3 J - V characteristics for ITO/MoO₃ (1 nm)/NPB (80 nm)/MoO₃ (5 nm)/Al device and ITO/NPB (80 nm)/ MoO₃ (5 nm)/Al device. The solid lines represent SCLC and TCLC, respectively.

NPB interfaces.

3.2.3 Photovoltaic performance

To further study the actual mechanism of MoO₃ layer in enhancing the device performance, photovoltaic experiments were conducted to measure the open circuit voltage. As shown in Fig. 4, V_{oc} drastically increases from 0.25 V to 1.1 V as the thickness of MoO₃ film increases from 0 to 20 nm. This means that built-in potential increases between ITO anode and Al cathode with the introduction of MoO₃. The V_{oc} reaches 0.8 V for the device with the insertion of only 1 nm MoO₃ layer. It is demonstrated that the work function of ITO can be changed by an ultra-thin layer due to interfacial dipoles, which enable modification of the electrode contact property, redistribute the electronic state at the interface and lead to a significant shift of the vacuum level. The conclusion may refer to the reports of Campbell *et al.*^[17] and Peisert *et al.*^[18]. The V_{oc} value of 1.1 V is close to the maximum value estimated from the energy difference between the ionization potential 5.4 eV of MoO₃ and the work function 4.3 eV of Al metal for the 20 nm MoO₃ device. In addition, although insertion of a MoO₃ layer can effectively lower the barrier energy for hole injection, thicker MoO₃ layer (>20 nm) may introduce series resistance into the device, leading to lower V_{oc} and efficiency after being beyond

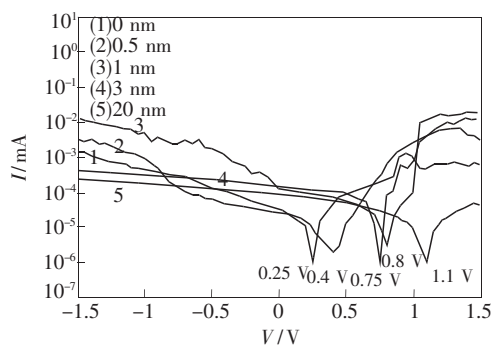


Fig. 4 Photovoltaic measurements for the devices with different MoO₃ thickness

an optimal thickness.

4 Conclusion

In summary, OLEDs based on MoO₃ as a buffer layer on ITO were fabricated. The device with 1 nm-thick MoO₃ shows the best performance, that is, the efficiency improvement as much as 1.6 times is observed. Capacitance-voltage measurements demonstrate that the hole injection is enhanced in low operational voltage through the addition of MoO₃. Results of the hole-only devices reveal that ohmic hole injection is formed at ITO/MoO₃/NPB interface. Photovoltaic measurements confirm that the improved hole injection is due to the reduction of barrier height, which is resulted from the addition of transition metal oxide.

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MoO_3 作空穴注入层的有机电致发光器件

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摘要: 研究了三氧化钼(MoO_3)薄层作为有机电致发光器件空穴注入层的器件性能和注入机制。发现 1 nm 厚度下发光器件性能最佳,器件的最大电流效率比对比发光器件的最大电流效率提高 1.6 倍。器件的电容曲线表明 MoO_3 薄层能有效提高空穴载流子的注入,多数载流子开始注入的拐点大约降低了 9 V。单空穴载流子电流曲线说明 MoO_3 器件的电流注入是空间电荷受限电流注入机制, MoO_3 使阳极界面处形成欧姆接触,而对比器件的电流注入是陷阱电荷受限电流注入机制。器件的光伏曲线进一步说明器件性能的提高是由于 MoO_3 层能使阳极界面能级分布发生改变,1 nm MoO_3 厚度下器件的内建电势从对比器件的 0.25 V 提高到了 0.8 V,有效降低了空穴注入势垒,提高了器件性能,但过厚的 MoO_3 层由于增加了器件的串联内阻,会导致器件性能降低。

关键词: 有机电致发光; 三氧化钼; 电容测量; 欧姆注入; 光伏测量

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