Low driving voltage in an organic light-emitting diode using MoO_3/NPB multiple quantum well structure in a hole transport layer*

Mu Xue(穆 雪)[a), Wu Xiao-Ming(吴晓明)[a)†], Hua Yu-Lin(华玉林)[a)], Jiao Zhi-Qiang(焦志强)[a)], Shen Li-Ying(申利莹)[a)], Su Yue-Ju(苏跃举)[a)], Bai Juan-Juan(白娟娟)[a)], Bi Wen-Tao(毕文涛)[a)], Yin Shou-Gen(印寿根)[a)], and Zheng Jia-Jin(郑加金)[b)]

[a)] *School of Materials Science and Engineering, Key Laboratory of Display Materials and Photoelectric Devices, Ministry of Education, Tianjin Key Laboratory of Photoelectric Materials and Devices, Tianjin University of Technology, Tianjin* 300384, *China*

[b)] *College of Optoelectronics Engineering, Nanjing University of Posts and Telecommunications, Nanjing* 210003, *China*

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The driving voltage of an organic light-emitting diode (OLED) is lowered by employing molybdenum trioxide (MoO_3)/N, N'-bis(naphthalene-1-yl)-N,N'-bis(phe-nyl)-benzidine (NPB) multiple quantum well (MQW) structure in the hole transport layer. For the device with double quantum well (DQW) structure of ITO/ [MoO_3 (2.5 nm)/NPB (20 nm)]$_2$/Alq_3(50 nm)/LiF (0.8 nm)/Al (120 nm)], the turn-on voltage is reduced to 2.8 V, which is lowered by 0.4 V compared with that of the control device (without MQW structures), and the driving voltage is 5.6 V, which is reduced by 1 V compared with that of the control device at the 1000 cd/m^2. In this work, the enhancement of the injection and transport ability for holes could reduce the driving voltage for the device with MQW structure, which is attributed not only to the reduced energy barrier between ITO and NPB, but also to the forming charge transfer complex between MoO_3 and NPB induced by the interfacial doping effect of MoO_3.

Keywords: organic light-emitting devices, low driving voltage, multiple quantum wells, charge transfer complex

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1. Introduction

Since the milestone work of the organic light-emitting diode (OLED) with high brightness using tris(8-hydroxyquinolinato)aluminum (Alq_3) as an emitting layer at low bias voltage was reported by Tang and Van Slyke in 1987,[1] the OLED has become an attractive field because of its application in panel display.[2–5] However, the power consumption of OLEDs needs to be reduced further to compete with other displays, and a low driving voltage is required to achieve low power consumption in these devices.[6] Currently, there are many ways to reduce the driving voltage of the OLED. The most common method is to use a p-type or n-type doping structure in a charge transport layer. For example, as an efficient buffer layer, molybdenum trioxide (MoO_3) is also used as a p-type dopant to lower the driving voltage.[7] However, the doping process is complicated and the minor doping ratio is inaccurate to control based on the co-evaporation method. The other method is to insert a buffer layer between the electrode and the organic transport layer, and some metal oxides with high work function have been reported to be able to improve the injection of holes, such as NiO_x and V_2O_5,[8,9] which is limited to lowering the driving voltage remarkably. In this work, we develop the non-doped multiple quantum well (MQW) structure in hole transport layer, which can improve the current density and luminance with a low driving voltage for the device. The hole transport layer (HTL) is configured with MoO_3/NPB MQW structure, and the effect of this MQW structure on the performance of the OLED was studied based on the reduction of energy barrier and the effect of interface doping.

2. Experiment

All devices are fabricated on glass substrates, each of which is coated with an indium–tin–oxide (ITO) anode layer with a sheet resistance of 20 Ω/sq. The cleaning of ITO glass is subsequently performed with detergent, deionized water, acetone, and isopropanol in an ultra-sonic bath for 15 min each. The structures of different devices are listed as follows:

A: ITO/NPB (40 nm)/Alq_3 (50 nm)/LiF (0.8 nm)/Al (120 nm);

B: ITO/MoO_3 (x nm)/NPB (40 nm)/Alq_3 (50 nm)/LiF (0.8 nm)/Al (120 nm);

C: ITO/[MoO_3 ($x/2$ nm)/NPB (20 nm)]$_2$/Alq_3 (50 nm)/LiF (0.8 nm) Al(120 nm);

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†Corresponding author. E-mail: wxm@mail.nankai.edu.cn

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D: ITO/[MoO_3 ($x/3$ nm)/NPB (13.3 nm)]$_3$/Alq_3 (50 nm)/LiF 0.8 nm)Al (120 nm).

The device with MQW structure consist of MoO_3 and NPB alternate layers in which the layer thickness of MoO_3 varies from x nm to $x/3$ nm and that of NPB varies from 40 nm to 13.3 nm (the value of x is the optimal thickness of MoO_3).

Each of the organic layers, as well as LiF and Al, is deposited on a pre-cleaned ITO glass substrate by using a thermal evaporation of BOC Edwards Auto 500 thermal evaporation coating system in an M. Braun 20 G glove box (made in Germany & England) at a pressure of about 2×10^{-4} Pa, The deposition rates and thicknesses of the various layers are monitored using a quartz crystal oscillator. The evaporation rates are 0.1 nm/s–0.3 nm/s, 0.1 nm/s, 0.05 nm/s, and 1 nm/s for the organic layers, the MoO_3 layer, the LiF layer, and the Al cathode, respectively. The current density–voltage–luminance (J–V–L) characteristics of the devices are simultaneously measured using a PR650 spectra scan spectrometer with a Keithley model 2400 programmable voltage–current source (made in America). All the measurements are carried out at room temperature in air without encapsulation.

3. Results and discussion

MoO_3 is usually used as an efficient buffer layer of an OLED near to the anode, which can not only reduce the operational voltage, but also enhance the brightness and power efficiency of the OLED. However, the thickness of MoO_3 can affect the electroluminescent performance of the device. At first, we fabricate a series of hole-only devices for optimizing the thickness of MoO_3. Figure 1 shows the current density–voltage (J–V) characteristics of the hole-only devices, and the inset shows one of the configurations of these devices, in which the thickness value x is determined to be 0 nm, 2 nm, 5 nm, and 8 nm, respectively. It is clearly shown that the current density of the device with a buffer layer is obviously higher than that of the device without a buffer layer at the same bias. When the driving voltage is more than 5.4 V, the device with 5-nm MoO_3 layer shows the most promising current density value in these devices. This indicates significantly that the injection of holes from ITO into the HTL becomes more effective for the case of the device with the MoO_3 buffer layer. However, in these devices, the over-thick MoO_3 buffer layer (the value $x > 5$ nm) may introduce series resistance into the hole-only device, which results in a low current density compared with that of the device with the optimal thickness of buffer layer.[10] From the J–V characteristics, we find that the optimal thickness is determined to be 5 nm ($x = 5$ nm).

On the other hand, the light-emitting devices, each of which consists of devices A (the control), B (single quantum well, SQW), C (double quantum well, DQW), and D (triple quantum well, TQW), are successfully fabricated to validate this effective approach. Figure 2 shows the current density–voltage–luminance (J–V–L) characteristics of all devices. The device with quantum well (QW) structure exhibits much higher brightness compared with that of the control device without QW structure at the same driving voltage. Moreover, the turn-on voltage of device C is 2.8 V which is reduced by 0.4 V compared with that of device A. At a brightness value of 1000 cd/m^2, the driving voltages of devices B, C, and D are 5.8 V, 5.6 V, and 6.2 V respectively, which are all lower than that of device A (1000 cd/m^2 at 6.6 V). Accordingly, it is obvious that the driving voltage of the Alq_3-based device could be reduced by 1.0 V at 1000 cd/m^2 through introducing the DQW structure into the hole transport layer. The inset in Fig. 2 shows the normalized electroluminescence (EL) spectra of devices A, B, C, and D at a fixed bias of 4 V. It can be seen that the four types of devices exhibit the same EL spectra, which could be attributed to the light emission from Alq_3, and it indicates that the recombination zone in EML could not be changed by the introduction of MQW structure in the device.

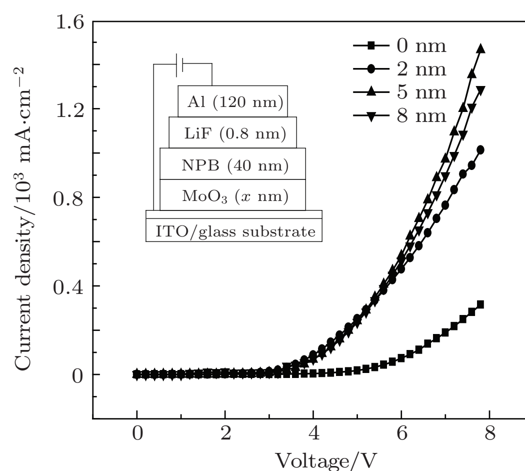

Fig. 1. Current density–voltage (J–V) characteristics of the hole-only devices, with inset showing the configuration of a hole-only device.

The J–V characteristics of devices A, B, C, and D are all presented in Fig. 2. It can be seen that the current density of the MQW device is higher than that of the control device. The increase in current density for device B is attributed to the abrupt shift of potential due to the formation of the interfacial dipole between the ITO anode and the MoO_3 buffer layer.[10,11] Simultaneously, instant electron transfer from ITO to MoO_3 at the interface should occur, which would result in the formation of a dipole layer at the interface. As a result, there will be an abrupt shift of potential across the dipole layer, which would lead to the up-shift in vacuum level.[10–13] Therefore, the energy barrier of hole injection is greatly reduced between the ITO and organic layer by this route, and the ability of hole injection can be improved. Accordingly, there is an increase in current density of device B. In other words, the MoO_3 in-

terfacial layer reduces the driving voltage of the OLED at the same brightness.

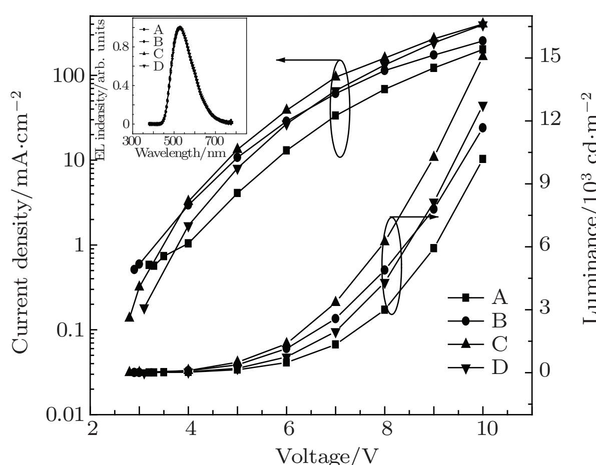

Fig. 2. Current density–voltage–luminance (J–V–L) characteristics of OLEDs with different quantum wells, with inset showing the normalized EL spectra of the devices A, B, C, and D at a driving voltage of 4 V.

Furthermore, also shown in Fig. 2, there is an obvious increase in luminance and current density of the device C compared with those of devices B and A at the same driving voltage. In this work, MoO_3 and NPB are alternate layers in the MQW structure, and the ultrathin film MoO_3 will form the effect of interfacial doping with NPB.[14] It could be explained by the partial p-doping effect of the buffer film layered with the HTL, which can facilitate the transport of the holes. It is already reported that MoO_3 is an effective p-dopant in NPB.[15] Partial p-doping of MoO_3 with NPB may increase the current density in the device. The increase of current density is mainly due to the complex form of charge transfer between MoO_3 and NPB. The energy level diagram of devices is shown in Fig. 3, similar highest occupied molecular orbital (HOMO) levels of MoO_3 and NPB are -5.3 eV and -5.4 eV, respectively. So the electrons can be transferred from the HOMO level of NPB to that of MoO_3 under the bias. At the same time, the NPB molecule could form the cation NPB^+ by losing part of the electrons, while the MoO_3 gained the electrons (which could also accumulate in this layer) to form the anion MoO_3^-, then the charge transfer complex MoO_3^-:NPB^+ could be formed by this route, in which the internal electric field may exist between the two layers (the direction of electric field is shown in Fig. 3). The internal electric field could reduce the injection energy barrier between the anode transport layer NPB and the hole transport layer NPB (adjacent to EML) for holes which would further facilitate its injection ability.[16] In addition, the charge transfer complex results in the increase of free holes between ITO and NPB, which can improve the conductivity of the HTL.[17–19] As a result, the current density of device C can be increased, and the driving voltage of the device can also be reduced simultaneously.

For device D, the increase in current density can also be ascribed to the effect of interfacial dipole and interfacial doping between MoO_3 and NPB. However, with the thickness of MQW kept unchanged, the interfaces between MoO_3/NPB will be more than those of other devices. The excessive effective interfaces will generate the restriction on the injection and transport of the holes, resulting in reductions in the current density and luminance of device D[20] (in Fig. 2). Therefore, the current density and luminance of device D are lowered compared with those of device C. On all accounts, of the four types of structures, the Alq_3-based device with DQW structure presents the most excellent electroluminescent performance, i.e., it has a turn-on voltage of 2.8 V, a lower driving voltage of 5.6 V at the 1000 cd/m^2, and a maximum brightness of 15060 cd/m^2 at 10 V.

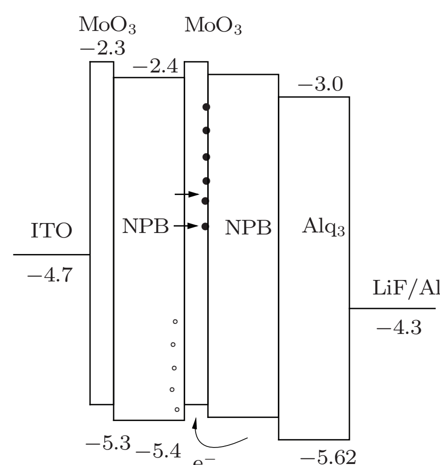

Fig. 3. Energy level (in units of eV) diagrams of the devices with the DQW structures, with dot representing the negative charge and circle denoting positive charge.

Table 1. Values of turn-on voltage $V_{turn-on}$, maximum current efficiency η_c, and power efficiency η_p of devices A, B, C, and D.

Devices	Turn-on voltage $V_{turn-on}$/V	Maximum current efficiency η_c/(cd/A)	Maximum power efficiency η_p/(lm/W)
A	3.2	5.05	2.23
B	2.9	4.59	2.38
C	2.8	3.91	2.98
D	3.1	3.35	2.09

The values of the turn-on voltage, the maximum current efficiency, and the power efficiency of the four devices are listed in Table 1. It could be seen that the QW device presents a low peak value of current efficiency compared with that of the control device, while the device with DQW structure indicates that the maximum power efficiency is improved by 33.6% (2.98 lm/W) compared with that of the control device (2.23 lm/W). As is well known, the power efficiency depends on carrier injection and transport, while current efficiency relies not only on the carrier injection but also on the carrier balance in the EML.[21] Although the QW structure can enhance

the injection and transport ability for holes in an OLED, the excess holes would still result in the imbalance of electron-hole pairs in the EML, which leads to a lower current efficiency.

4. Conclusions

In this paper, the current density and luminance of the device can be improved by the MQW structures of MoO_3 and NPB used as the hole transport layer. The driving voltages of these devices can be reduced markedly, which is mainly attributed to the effect of interfacial dipole and interfacial doping between MoO_3 and NPB. The device with DQW structure presents a turn-on voltage of 2.8 V and a lowest driving voltage of 5.6 V at 1000 cd/m^2. The result indicates that this approach has a significant value of commercialization application, which may be a potential to fulfill the requirements of low driving voltage for an OLED.

References

[1] Tang C W and VanSlyke S A 1987 *Appl. Phys. Lett.* **51** 913
[2] Li W, Wei X, Yu L, Jun W Y and Yu C D 2011 *Displays.* **32** 45
[3] Yu J S, Suo F, Li W Z, Li H, Li L and Jiang Y D 2007 *Acta Phys. Chim. Sin.* **23** 1821 (in Chinese)
[4] Tang X Q, Yu J.S, Li L, Wang J and Jiang Y D 2008 *Acta Phys. Chim. Sin*. **24** 1012 (in Chinese)
[5] Meng L C, Lou Z D, Yang S Y, Hou Y B, Teng F, Liu X J and Li Y B 2012 *Chin. Phys.* B **21** 088504
[6] Kyoung S Y and Jun Y L 2009 *Synth. Met.* **159** 69
[7] Li L S, Guan M, Cao G H, Li Y Y and Zeng Y P 2012 *Displays.* **33** 17
[8] Wei B, Yamamoto S, Ichikawa M, Li C, Fukuda T and Taniguchi Y 2007 *Semicond. Sci. Technol.* **22** 788
[9] Zhang H M and Wallace C H 2008 *IEEE Trans. Electron. Dev.* **55** 2517
[10] Hou L T, Liu P Y, Zhang J L, Wu C H, Li Y W and Wu B 2010 *Chin. J. Lumin*. **31** 326 (in Chinese)
[11] Wang F X, Qiao X F, Xiong T and Ma D G 2008 *Org. Electronics* **9** 985
[12] Zhang D D, Feng J, Liu Y F, Zhong Y Q, Bai Y, Jin Y, Xie G H, Xue Q, Zhao Y, Liu S Y and Sun H B 2009 *Appl. Phys. Lett.* **94** 223306
[13] Toshinori M, Yoshiki K and Hideyuki M 2007 *Appl. Phys. Lett.* **91** 253504
[14] Liu G Q, Ji W Y, Xie W F and Zhang H Z 2011 *Spectroscopy and Spectral Analysis* **31** 882 (in Chinese)
[15] Li L S, Guan M, Cao G H, Li Y Y and Zeng Y P 2010 *Appl. Phys.* A **99** 251
[16] Riel H, Brütting W, Beierlein T, Haskal E, Müller P and Rieß W 2000 *Synth. Met.* **111–112** 303
[17] Zhang D D, Feng J, Chen L, Wang H, Liu Y F, Jin Y, Bai Y, Zhong Y Q and Sun H B 2011 *IEEE J. Quantum Electron.* **47** 591
[18] Hamwi S, Meyer J, Winkler T, Riedl T and Kowalsky W 2009 *Appl. Phys. Lett.* **94** 253307
[19] Shin W J, Lee J Y, Kim J C, Yoon T H, Kim T S and Song O K 2008 *Org. Electronics* **9** 333
[20] Ju H N, Xu Z, Zhao S L, Zhang F J, Kong C, Yan G and Gong W 2011 *Acta Phys. Sin.* **59** 8093 (in Chinese)
[21] Haq K, Khan M A, Zhang X W, Zhang L, Jiang X Y and Zhang Z L 2010 *J. Non-Cryst. Solids* **356** 1012