Short Communication

Low operating-voltage and high power-efficiency OLED employing MoO3-doped CuPc as hole injection layer

Linsen Li a, Min Guan a,*, Guohua Cao b, Yiyang Li b, Yiping Zeng b

a Key Laboratory of Semiconductor Materials Science, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China
b Material Science Center, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

1. Introduction

During the last two decades, organic light-emitting diodes (OLEDs) have attracted much attention owing to their promising applications in the fields of next generation solid-state lighting and flat-panel display [1–5]. To realize low driving voltage and high efficiency of OLEDs, many efforts are done to design the appropriate configuration for carrier injection and transportation [6–11]. For example, inserting a thin hole injection layer (HIL) between indium tin oxide (ITO) and hole transportation layer (HTL), which will reduce the energy barrier to enhance hole injection, ultimately depress the driving voltage and improve power efficiency. Besides, the hole mobility in organic material is generally larger than electron mobility, so hole block layer and electron block layer are introduced to balance the holes and electrons in the emitting layer for the high current efficiency.

Recently, transition metal oxide (e.g., MoO3 [8,9], NiO [10], RuOx [11], etc.) with high work function and strong molecular electronegativity, have been used as individual HIL. Furthermore, MoO3 has been reported as an effective p-dopant in NPB to improve the device efficiency and lower the driving voltage [12]. Copper phthalocyanine (CuPc), is the most commonly used as hole injection layer in OLEDs, and it is found the utilization of CuPc improved the device efficiency. However, the insertion of CuPc often leads to substantial increase in device operational voltage [13]. In this letter, we found that MoO3-doped CuPc as HIL not only maintain the high current efficiency, but also significantly reduced the operation voltage and greatly enhanced the power efficiency of device.

2. Experiment

Fig. 1 shows the cross-section chart of the device structure. All the devices were fabricated on ITO coated glass with a sheet resistance of 30 Ω/sq in an organic molecular beam deposition system (OMBD) with the vacuum about 3 × 10−7 torr, and all the deposition experiments were continued without vacuum break. Prior to the organic films deposition, the substrates were treated by UV-ozone for 15 min to enhance the work function of ITO. N,N-bis-(1-naphthyl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H, 11H-(1)-benzopyropyrano(6,7,8-ij)quinolizin-11-one (C545T); tris(8-hydroxyquinoline) aluminum (Alq3)/Alq3/LiF/Al shows the driving voltage of 4.4 V, and power efficiency of 4.3 lm/W at luminance of 100 cd/m2. The charge transfer complex between CuPc and MoO3 plays a decisive role in improving the performance of OLEDs. The AFM characterization shows that the doped film owns a better smooth surface, which is also in good agreement with the electrical performance of OLEDs.

© 2011 Elsevier B.V. All rights reserved.
measured by a ST-86LA spot photometer and a computer controlled Keithley electrometer 2400 at room temperature in ambient atmosphere. The optical absorption spectra of organic thin films were obtained from the UV–visible spectrometer (UV-3100). Veeco NanoScope 3D atomic force microscope (AFM) measurements were performed to characterize the surface morphology of the MoO3-doped CuPc films.

3. Results and discussion

Fig. 2 shows the J–V–L characteristics of various OLEDs listed in Table 1. The devices with MoO3-doped CuPc have the lower operating voltage than the one with individual CuPc as HIL. For example, the devices B, C and D show the operating voltages of 5.5 V, 4.4 V, and 4.6 V at the luminance of 100 cd/m², respectively. In contrast, the devices A with individual CuPc show the operating voltage of 8.1 V at the same luminance. These results indicate that the doped layer effectively enhances the hole injection and transport. However, device E with individual MoO3 own operating voltage of 5.0 V at the luminance of 100 cd/m². It can be concluded that these results are attributed to the amount of a formative charge transfer (CT) complex between CuPc and MoO3 (MoO3/CuPc+).

The CT complex can enhance the electrical productivity of the doped layer and promote the hole injecting and transporting like the interface dipole, which will decrease the operating voltage and increase the efficiency. The operating voltage of the device is reduced with the increase of doping concentration of MoO3 and reaches to optimum value at 50 V% MoO3 doping conditions, then the quantity of CT complex decreases with a further increase of MoO3 doping concentration, so the operating voltage of the device finally shifts to a higher value. The UV–visible spectra of the doped films also prove it.

Additionally, the current efficiency-current density-power efficiency characteristics of these devices are shown in Fig. 3. The transformation behavior of the current density-power efficiency characteristic of various OLEDs is the same as the J–V–L characteristics because of the amount of CT complex. For example, the device C with 50 V% MoO3-doped CuPc as HIL exhibit the best
performance, the power efficiency of 4.3 lm/W have been achieved at luminance of 100 cd/m². However, the device A with individual CuPc as HIL and device E with individual MoO₃ as HIL exhibit the lower power efficiency of 0.95 lm/W, and 1.48 lm/W at the same luminance, respectively. Nevertheless, the transformation trend of the current density – current efficiency characteristic has a little difference with the J–V–L characteristics. Especially, the device A and device C achieve the best current efficiency of 7.2 cd/A at current density of 200 mA/cm², which is larger than the other devices.

As mentioned in the introduction, OLED with CuPc as HIL can achieve the high current efficiency by sacrificing the operating voltage, that is why the device A owns the poor power efficiency. To sum up, the device C with the optimal doping ratio of 50 V% MoO₃: CuPc as HIL obtains the best performances.

As we know, if appropriate configuration and energetic level exist in the different molecules, a CT complex can be easily formed by co-evaporation [14]. Here, CuPc has a HOMO level of 5.2 eV [13] and MoO₃ has a work function of about 5.43 eV, [15], thus the CT complex can be formed between CuPc and MoO₃(MoO₃/CuPc). And the formed CT complex must have the different molecule orbit after overlapping of the electron clouds. That is to say, MoO₃ will affect π-orbit energy of CuPc in the doped layer. Meanwhile, the UV–visible spectra normally shows the transition from π-orbit to π'-orbit over the range from 200 to 800 nm. Fig. 4 plots the UV–visible spectra of CuPc, 20 V% MoO₃-doped CuPc, 50 V% MoO₃-doped CuPc, 66 V% MoO₃-doped CuPc, MoO₃, and MoO₃ + CuPc films on quartz substrates. With the increase of MoO₃ doping concentration, the two strong absorption peaks of CuPc has shifted to long wavelength and the absorption intensity has changed. For example, the left absorption peak of CuPc has shifted from 622 nm to 684 nm in the 50 V% MoO₃-doped CuPc film, and the intensity of left peak is weakened comparing with the right peak of CuPc. However, the spectrum of MoO₃ + CuPc by adding the spectra of MoO₃ to CuPc shows no red shift. It indicates that the transition from π-orbit to π'-orbit in doped layer is different from original transition in CuPc film. In conclude, we believe that the redshift is attributed to the formation of a CT complex (MoO₃/CuPc). When MoO₃ accept electron from the CuPc, the transition energy from π-orbit of CuPc to π'-orbit is decrescent, so the UV–visible spectra show the red shift. This result is similar to those on CT complexes discussed in other literature [14]. For proving the existence of the CT complex, device F with MoO₃ 2.5 nm/CuPc 2.5 nm as HIL was fabricated. It is clear that device F own poor performances in operating voltage and power efficiency because no CT complex exists in the HIL.

Fig. 5 shows AFM images of CuPc, 50 V% MoO₃-doped CuPc, and MoO₃ films on glass substrates. The thicknesses of all thin films are about 50 nm. The surface root-mean-square (RMS) roughness of the CuPc, 50 V% MoO₃-doped CuPc, and MoO₃ films are 2.52 nm, 0.94 nm and 2.06 nm, respectively. The better smooth surface of the doped layer can be attributed to the fact that its two kinds of molecules mutually fill the gaps between them by the co-evaporation and the doped film provides the next deposition with a smoother surface which helps to improve the ultimate device stability.

4. Conclusions

In summary, we demonstrated high power efficiency and low operating voltage for OLED with MoO₃-doped CuPc layer as HIL. The optimal doping ratio is 50 V% MoO₃: CuPc for forming the most CT complex between CuPc and MoO₃. The CT complex confirmed by peak red shift of UV–visible spectra plays a decisive role in improving the performances of OLEDs. The AFM characterization show the doped film owns a better smooth surface which is also in good agreement with the electricity performance of OLEDs.

Acknowledgments

We acknowledge the supports from National Natural Science Foundation of China (NNSFC 60876043) and the Knowledge Innovation Program of the Chinese Academy of Sciences (ISCAS2008T11).

References