APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 15 12 APRIL 2004

Dual role of LiF as a hole-injection buffer in organic light-emitting diodes

J. M. Zhao, S. T. Zhang, X. J. Wang, Y. Q. Zhan, X. Z. Wang, G. Y. Zhong, Z. J. Wang, X. M. Ding, W. Huang, and X. Y. Hou[a]
Surface Physics Laboratory (National Key Laboratory), Institute of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China

(Received 3 November 2003; accepted 10 February 2004)

It is demonstrated experimentally that the effect of a LiF buffer layer inserted at the ITO\N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′ biphenyl 4,4′-dimaine (NPB) interface on the hole injection is greatly dependent on the initial barrier height (IBH) existing at the interface. Only for a large IBH, will the introduction of the LiF show improvement effect. For small one, it will weaken the hole injection. These phenomena are explained in terms of tunneling model and calculations based on this model show a good agreement with the experimental results. This further confirms that the energy level realignment and the change in carrier tunneling probability are mainly responsible for the variation of current injection induced by the insulating buffers in organic light-emitting diodes. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695444]

Since the first demonstration of the highly efficient electroluminescence from organic light-emitting diodes (OLEDs),[1] much effort has been made to improve their performance.[2–13] It has been found that the introduction of thin layers of insulating buffers, including LiF, NaCl, alkali metal acetates, CsF, poly(methyl methacrylate) (PMMA), Al_2O_3, sodium stearate,[2–8] between electrodes and organic layers, is an effective way to enhance the current injection and lower the operating voltage. In the case of using LiF or CsF as the buffer, dissociation of the alkali halide and subsequent ‘‘doping’’ of the alkali into the organic was suggested as a possible mechanism leading to the enhanced electron injection.[9] More recently, hole-injection enhancement induced by insulating buffers was also realized. For example, LiF[10] and SiO_2[11] with proper thicknesses deposited on indium-tin oxide (ITO) anode improved the hole injection to poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) and N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′ biphenyl 4,4′-dimaine (NPB). However, a report by Zhao *et al.* indicated that LiF on ITO weakened the hole injection to N,N′-diphenyl-N,N′-bis(3-methylphenyl)1-1′biphenyl-4,4′ diamine (TPD) in a considerable voltage range.[12] This means the existence of an insulating buffer layer, even in optimized thickness, may not always be beneficial to the operation of OLEDs. A thorough investigation into the dependence of the buffer behavior on the initial interface properties is therefore needed.

In this letter, we show a strong evidence that the effects of LiF inserted at the ITO\NPB interface on the hole injection are greatly dependent on the initial barrier height (IBH) existing at the interface. The introduction of the LiF buffer will enhance the hole injection when the IBH is large. On the contrary, for small IBH it will weaken the hole injection compared with the case of the bare ITO. These phenomena are explained in terms of tunneling model[6] and calculation based on this model shows a good agreement with the experimental ones. This further confirms that the energy level realignment and the change in carrier tunneling probability[6,13] are mainly responsible for the variation of current injection induced by the insulating buffers in OLEDs.

Two types of OLEDs by different ITO treatments, namely, UV ozone and H_2 plasma, were experimentally fabricated with the same device structure of ITO\LiF\NPB\tris(8-hydroxyquinoline) aluminum(Alq_3)\LiF\Al. The devices fabricated with UV-ozone processed ITO are termed as O-OLEDs and those with H_2-plasma processed ITO as H-OLEDs. Neither of the treatment methods used here changes the bulk properties (sheet resistance and transmittance) of ITO. The main difference resulting from them is that different surface terminations are formed in the two cases and hence the position of Fermi level, E_F, of ITO is lowered by UV-ozone treatment and raised by H_2-plasma one.[14] So, the hole-injection IBH of O-OLEDs is smaller than that of H-OLEDs when no LiF buffer is present between ITO and NPB.

Prior to film deposition, the ITO-coated substrates were cleaned using the routine procedure including ultrasonication in detergent and deionized water sequentially and a final UV ozone or H_2 plasma treatment. A multilayer structure of LiF (varied thickness)\NPB (65 nm)\Alq_3 (65 nm)\LiF (0.5 nm)\Al (200 nm) was sequentially deposited onto the cleaned ITO substrate. Here the LiF layer between Alq_3 and Al is for enhancing the electron injection.[2] During the fabrication process, a quartz-oscillator thickness monitor was used to detect the deposition rate. Organic and LiF films were deposited in an organic-molecule-beam-deposition chamber at a base pressure of 5.0×10^{-6} Pa with a deposition rate of 0.1–0.2 nm/s and 0.01 nm/s, respectively. Then the samples were exposed to air and transferred to another chamber, and finished by the evaporation of 200 nm Al with a deposition rate of 2–3 nm/s. Current–voltage ($I-V$) characteristics were recorded with a programmable voltage–current source (Keithley 236).

The $I-V$ curves of O-OLEDs and H-OLEDs with different-thickness LiF between ITO and NPB are shown in Fig. 1. To characterize more clearly the effects of the LiF

---

[a] Electronic mail: xyhou@fudan.edu.cn

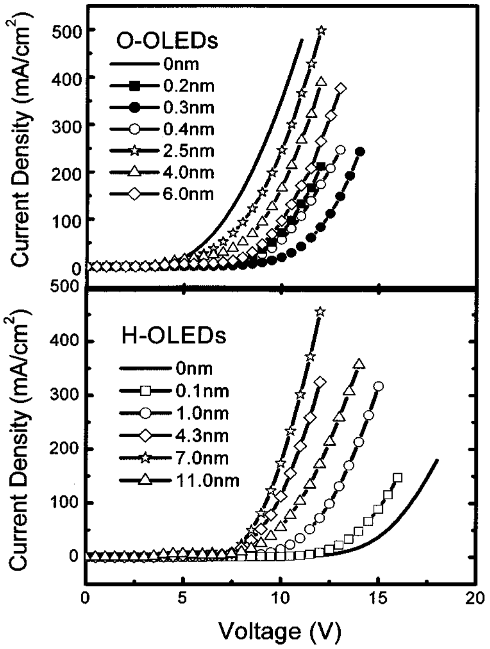

FIG. 1. $I-V$ curves measured from two types of OLEDs with a LiF buffer of various thicknesses inserted at their NPB/ITO interfaces.

buffer on the hole injection, the current density values at 5 V for O-OLEDs and at 10 V for H-OLEDs as a function of the LiF thickness are plotted in Fig. 2. It can be seen that the current characteristics of H-OLEDs are similar to those reported literatures.[2–8,10,11] That means the hole injection is increased with the thickness of the LiF buffer in the thin range (0.1–7.0 nm) and decreased gradually in the thick one (7.0–11.0 nm). Hence, there is an optimal thickness of 7.0 nm for the hole injection, which dramatically enhances the hole injection and reduces the operating voltage. However, the LiF-induced current variation of the O-OLEDs is quite different. The very thin (0.1–0.3 nm) layers of LiF quickly reduce the hole injection and then thick (0.3–2.5 nm) ones enhance them gradually and even thicker (>2.5 nm) ones reduce them again. Accordingly, there appears a worst thickness of 0.3 nm besides an optimal thickness of 2.5 nm for the hole injection. It is noticeable that even in the case of the optimal thickness, the current injection is still reduced compared with that of the bare ITO.

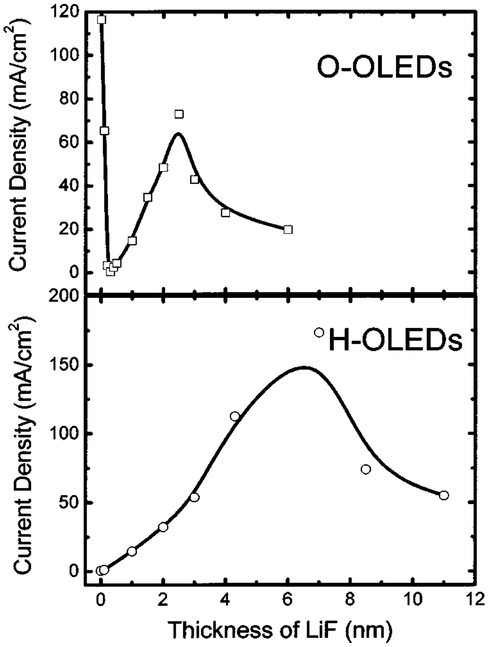

FIG. 2. Current density values measured from O-OLEDs biased at 5 V and from H-OLEDs at 10 V vs the thickness of LiF buffer.

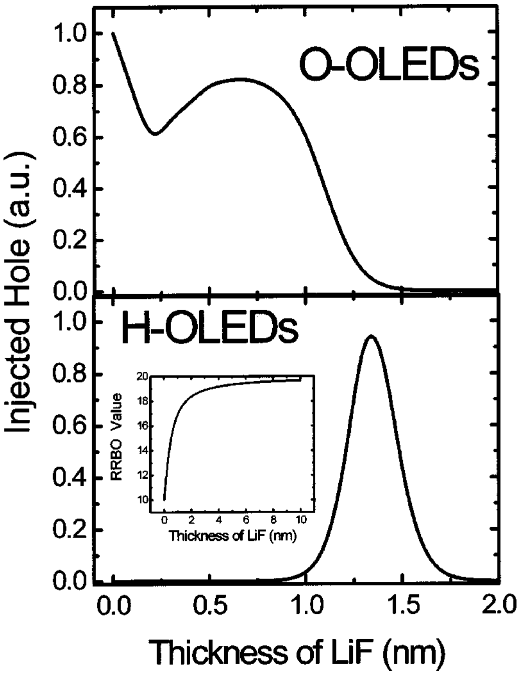

FIG. 3. Normalized number of injected holes calculated for O-OLEDs biased at 5 V and for H-OLEDs at 10 V vs the thickness of LiF buffer. Inset is the assumed curve of RRBO values vs LiF thicknesses.

As is apparent from the above results, compared with the case of the bare ITO, the hole injections are all weakened by the introduction of LiF in the range of 0.1–6.0 nm for O-OLEDs and enhanced in the range of 0.1–11.0 nm for H-OLEDs. As mentioned above, it is plausible that the different behavior of current injection of the two types of OLEDs induced by the LiF buffers are related to the different E_F positions at the ITO surfaces resulted from different atomic terminations.

More recently, Zhang *et al.*[13] at this laboratory made a detailed calculation based on tunneling theory, showing that various parameters, such as resistivity ratio of buffer to organic layers (RRBO), the position of the conduction band minimum of the buffer relative to the lowest unoccupied molecular orbital (LUMO) of the organic layer and the thicknesses of both layers, may affect the electron injection in the system of electrode/buffer/organic layer. However, the position of E_F of the electrode was not taken into consideration in that calculation. Moreover, a constant RRBO independent of the buffer layer thickness was assumed there. The work of Yoon *et al.*[15] indicates that the value of RRBO is dependent on the buffer thickness, rather than a constant value for all the thicknesses as were used previosly.[13] According to this, thickness-dependent RRBO as shown in the inset of Fig. 3 is adopted and calculations for the two types of OLEDs with different E_F of ITO are carried out based on that model. For simplicity, a single organic layer system of ITO\LiF\NPB is chosen as the model. The parameters used in the calculation are: the highest occupied molecular orbital (HOMO) of NPB

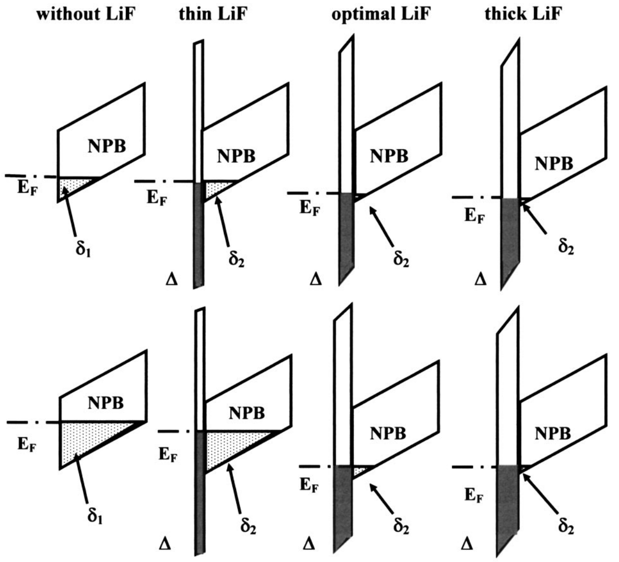

FIG. 4. Schematic diagram of the tunneling model without and with a LiF buffer of different thicknesses. Upper is the cases of O-OLEDs and lower is those of H-OLEDs.

was set as −5.2 eV from the vacuum level,[16] the valence band maximum of LiF as −8.0 eV, which was measured using UPS, the thickness of NPB as 180 nm considering the large potential drop across the Alq_3 layer,[17] and the E_F of ITO as −4.7 eV for O-OLEDs and −4.0 eV for H-OLEDs,[14] respectively. Figure 3 shows the calculated results of O-OLEDs at 5 V and H-OLEDs at 10 V, respectively. By comparing Figs. 2 and 3 it can be seen clearly that there are good agreements between the experimental results and calculated ones in: (i) the overall structures of the curves for the two types of OLEDs and (ii) H-OLEDs showing the larger optimal thickness than O-OLEDs. However, the absolute values of experiments and calculations disagree with each other yet, which may be attributed to the simplicity of the model.[13]

Figure 4 is the schematic diagram of LiF playing the different roles in the two types of OLEDs based on the energy level realignment and tunneling model, in which the tunneling barriers of hole are represented by the shaded area. If no buffer layer is included, upon application of a forward voltage the hole must tunnel through the triangle barrier, denoted by δ_1. The presence of LiF has two effects: (a) the voltage drop across it lowers the ITO E_F by the same amount and hence reduces the triangle barrier in NPB layer, then δ_1 becomes δ_2; (b) add an additional barrier formed by itself, denoted by Δ. So, whether the introduction of LiF can enhance the hole injection or not is determined by the relative magnitude of δ_1 and the total effective barrier of $\Delta+\delta_2$. If $\delta_1>\Delta+\delta_2$, the hole injection will be enhanced and if $\delta_1<\Delta+\delta_2$ it will be reduced. In the case of O-OLEDs, the IBH at the ITO\NPB interface is small due to the high work function of ITO. Therefore, for very thin LiF layers with small RRBOs, the effect (a) is not evident, as shown in Fig. 4. It can be approximately regarded as $\delta_1\approx\delta_2$, and thus, $\delta_1<\Delta+\delta_2$. With the increase of LiF thickness, effect (a) will be prominent due to its large RRBOs and hence large voltage drops. So, the $I-V$ curves will shift toward the lower voltage direction. Over the optimal thickness of LiF, δ_2 will hardly vary but Δ increase quickly with the thickness of LiF, and hence the $I-V$ curves will shift toward the higher voltage direction again. In the case of H-OLEDs, due to the large width of δ_1, a bit lower of E_F will lead to its considerable reduction. However, upon the introduction of LiF, $\delta_1\gg\delta_2$, and hence $\delta_1>\Delta+\delta_2$ will occur even for small RRBOs associated with thin LiF layers. As the H-OLEDs show, in a wide range of LiF thickness, the hole injection is improved since the large δ_1 leads to effect (a) evident. Of course, too thick LiF will still lead to $\Delta+\delta_2>\delta_1$. To align the E_F of ITO and the HOMO of NPB for H-OLEDs, a larger voltage drop across LiF is a must due to the bigger difference between them. Therefore, the optimal thickness of H-OLEDs is larger than that of O-OLEDs.

In summary, we have shown strong evidence that the role of a LiF buffer playing in hole injection in ITO\NPB-based OLEDs is largely dependent on the IBH at ITO\NPB interface. Only for a large IBH, will the introduction of LiF show beneficial effect. For a small one, the presence of the LiF buffer will weaken the hole injection. These phenomena are explained in terms of tunneling model. These results may shed new light on the use of buffer layer in OLEDs.

This work is supported by the CNKBRSF, the National Natural Science Foundation of China under Grant No. 10174013 and the Science and Technology Commission of Shanghai Municipality.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] L. S. Hung, C. W. Tang, and M. G. Mason, Appl. Phys. Lett. **70**, 152 (1997).
[3] S. J. Kang, D. S. Park, S. Y. Kim, C. N. Whang, K. Jeong, and S. Im, Appl. Phys. Lett. **81**, 2581 (1997).
[4] C. Ganzorig, K. Suga, and M. Fujihira, Mater. Sci. Eng., B **85**, 140 (2001).
[5] P. Piromreun, H. S. Oh, Y. Shen, G. G. Malliaras, J. C. Scott, and P. J. Brock, Appl. Phys. Lett. **77**, 2403 (2000).
[6] Y. E. Kim, H. Park, and J. J. Kim, Appl. Phys. Lett. **69**, 599 (1996).
[7] F. Li, H. Tang, J. Anderegg, and J. Shinar, Appl. Phys. Lett. **70**, 1233 (1997).
[8] Y. Q. Zhan, Z. H. Xiong, H. Z. Shi, S. T. Zhang, Z. Xu, G. Y. Zhong, J. He, J. M. Zhao, Z. J. Wang, E. Obbard, H. J. Ding, X. J. Wang, X. M. Ding, W. Huang, and X. Y. Hou, Appl. Phys. Lett. **83**, 1656 (2003).
[9] G. Mason, C. W. Tang, L. S. Hung, P. Raychaudhuri, J. Madathil, D. J. Giesen, L. Yan, Q. T. Le, Y. Gao, S. T. Lee, L. S. Liao, L. F. Cheng, W. R. Salaneck, D. A. dos Santos, and J. L. Bredas, J. Appl. Phys. **89**, 2756 (2001).
[10] F. Zhu, B. Low, K. Zhang, and S. Chua, Appl. Phys. Lett. **79**, 1205 (2001).
[11] Z. B. Deng, X. M. Ding, S. T. Lee, and W. A. Gambling, Appl. Phys. Lett. **74**, 2227 (1999).
[12] Y. Zhao, S. Y. Liu, and J. Y. Hou, Thin Solid Films **397**, 208 (2001).
[13] S. T. Zhang, X. M. Ding, J. M. Zhao, H. Z. Shi, J. He, Z. H. Xiong, H. J. Ding, E. G. Obbard, Y. Q. Zhan, W. Huang, and X. Y. Hou, Appl. Phys. Lett. **84**, 425 (2004).
[14] C. C. Wu, C. I. Wu, J. C. Sturm, and A. Kahn, Appl. Phys. Lett. **70**, 1348 (1997).
[15] J. Yoon, J. J. Kim, T. W. Lee, and O. O. Park, Appl. Phys. Lett. **76**, 2152 (2000).
[16] C. H. Kim and J. Shinar, Appl. Phys. Lett. **80**, 2201 (2002).
[17] J. M. Simon, L. B. V. Geraldine, A. W. Matthew, and B. W. Alison, Org. Electr. **3**, 129 (2002).