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


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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), Al2O3, 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, LiF10 and SiO211 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-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 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 are mainly responsible for the variation of current injection induced by the insulating buffers in OLEDs.
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.

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 previously.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 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.

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was set as $-5.2$ eV from the vacuum level, 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, and the $E_F$ of ITO as $-4.7$ eV for O-OLEDs and $-4.0$ eV for H-OLEDs, 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 calculations disagree with each other yet, which may be attributed to the simplicity of the model.

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 $\delta_1$. 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 $\delta_1$ becomes $\delta_2$; (b) add an additional barrier formed by itself, denoted by $\Delta$. Therefore, upon the introduction of LiF, $\delta_1 \Rightarrow \delta_2$, and hence $\delta_1 \Rightarrow \Delta + \delta_2$ 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 $\delta_1$ leads to effect $\delta_1$ evident, as shown in Fig. 4. 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.

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