

Enhancement of electron injection in organic light-emitting devices using an Ag/LiF cathode

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A LiF-buffered silver cathode has been used in organic light-emitting devices (OLEDs) with structure indium-tin-oxide/N,N'-bis-(1-naphthyl)-diphenyl-1,1'-biphenyl-4,4'-diamine (50 nm)/Alq₃ (100 nm)/cathode. The efficiency of electron injection from the cathode is strongly dependent on the thickness of the LiF buffer layer. While a LiF layer thinner than 1.0 nm leads to higher turn-on voltage and decreased electroluminescent (EL) efficiency, a LiF layer of 3.0 nm significantly enhances the electron injection and results in lower turn-on voltage and increased EL efficiency. A brightness of 16 000 cd/m² and EL efficiency of 4.8 cd/A can be achieved with an Ag/LiF cathode. This dependence of electron injection on the LiF thickness is quite different from that reported for OLEDs with a Al/LiF cathode, but can be well understood using the tunneling model. © 2004 American Institute of Physics. [DOI: 10.1063/1.1655676]

To achieve excellent performance in organic light-emitting devices (OLEDs), it is desirable to use a low work function metal (Mg, Li, Ca, etc) or metal alloy (e.g., Mg:Ag) as the cathode. This gives a small effective injection barrier height at the organic/metal electrode interface. However, these metals or alloys are not well fit for the operation environment because of their relatively high chemical reactivity in air. If less active metals such as aluminum (Al), and silver (Ag) are used as the cathodes, however, the devices have given poor light output and low electroluminescent (EL) efficiency. In 1997, by inserting a thin buffer layer of LiF between Alq₃ and Al, a great enhancement in EL performance of OLEDs with these stable metals was first reported.¹ Thereafter, many insulating materials such as MgO, Al₂O₃, MgF₂, and NaSt were also found to be either suitable or effective buffers in small molecule-based OLEDs,¹⁻⁴ where the optimal thickness of the insulating layer was usually less than 1.0 nm. In the case of LiF as a buffer layer, Stobel *et al.*⁵ reported that among Mg, Ag, Ca, Li, and Al, only aluminum can be used as the effective cathode to improve the performance of OLEDs. A very poor electron injection of a device having 0.3 nm LiF between Alq and Ag cathode was also demonstrated by Hung *et al.*⁶ Recently, H. Heil *et al.*⁷ fabricated a device with a layer sequence of Ag/LiF (0.2 nm)/Alq₃ (200 nm)/LiF (0.2 nm)/Ag, which did not show any improved electron injection. Based on these ex-

perimental results in which the adopted thickness of LiF in the Ag/LiF cathode is mostly less than 1.0 nm, silver, a noble metal, has been so far judged as a poor cathode material to combine with a LiF buffer layer.

We nevertheless report the excellent EL performance of the devices containing a Ag/LiF cathode structure. The thickness of the LiF layer we adopted is varied in a range of 0–5.0 nm. The presence of an ultrathin LiF layer of 0.6 nm between Alq and Ag will lead to a poorer EL performance than that of the device without LiF. With the thickness of the buffer layer being further increased, however, the current injection is gradually improved. The device with a 3.0-nm-thick LiF layer exhibits excellent EL characteristic. A significantly reduced turn-on voltage, a brightness of 16 000 cd/m², and an EL efficiency of 4.8 cd/A, comparable to the results of the devices with an Al/LiF cathode,⁸ are achieved. The dependence of device performance on the LiF thickness is tentatively ascribed to the effect of electron tunneling through LiF layers.

Indium-tin-oxide (ITO)-coated glass with a sheet resistance of 20 Ω per square was used for the device fabrication. The routine cleaning procedure included sonication in detergent, rinsing in de-ionized water, and a final UV ozone treatment to remove remaining organic materials. During the fabrication process, a quartz-oscillator thickness monitor was used to detect the deposition rate. A multilayer structure of N,N'-bis-(1-naphthyl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (50 nm)/Alq₃ (100 nm)/LiF (0–5 nm)/Ag (110 nm) was sequentially deposited on the cleaned ITO substrate. The use of relatively thick Alq₃ layer in the device was for sure

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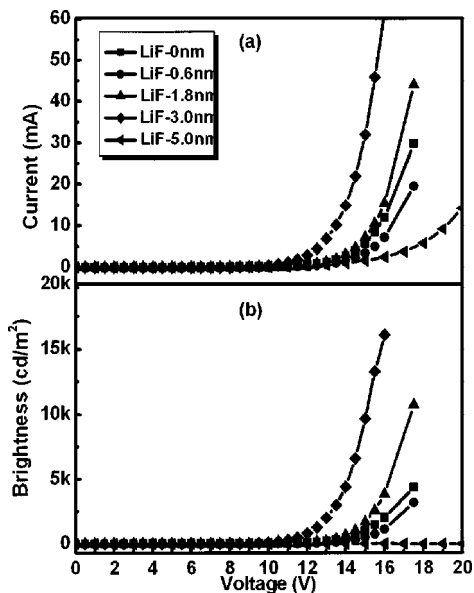


FIG. 1. (a) and (b): Current- and luminance-voltage characteristics of devices with different LiF layer thicknesses: 0 nm (square), 0.6 nm (circle), 1.8 nm (sitting triangle), 3.0 nm (diamond), and 5.0 nm (standing triangle).

of hole excess at the Alq₃/NPB interface so that any effect of the LiF thickness on electron injection might be readily detected. Organic films were deposited at a base pressure of 8.0×10⁻⁶ Pa with a deposition rate of 0.2–0.3 nm/s. LiF layers with different thicknesses in the range of 0–5.0 nm were deposited at 0.5–0.6 nm/min from a boron nitride crucible. The Ag cathodes were evaporated subsequently at 0.2 nm/s through a shadow mask. Luminance-current-voltage (*L-I-V*) characteristics were recorded simultaneously by combining the spectrometer with a programmable voltage-current source Keithley 236. All measurements were done in a nitrogen glovebox.

Current-voltage (*I-V*) and luminance-voltage (*L-V*) characteristics of the devices having a Ag/LiF cathode with different thicknesses of the LiF layer are shown in Figs. 1(a) and 1(b), respectively. It can be seen that there are apparent differences of *I-V* and *L-V* characteristics in devices. With a 0.6 nm LiF layer inserted between Alq₃ and Ag, both *I-V* and *L-V* curves are shifted towards the higher voltage region compared with the device without LiF. For instance, the turn-on voltage of this device, defined as the value of bias at which the current density is 1 mA/cm², is 11.3 V, while that for the device without LiF is 10.8 V. Similarly, the voltages to obtain a luminance of 1000 cd/m² for the devices with 0- and 0.6-nm-thick LiF are 14.2 and 15.9 V, respectively. The poor characteristics of the devices with a LiF layer thinner than 1.0 nm were reported in previous literature.⁵⁻⁷ However, with further increasing of the LiF layer thickness, current injection of the device is gradually enhanced. When the thickness of LiF is increased to 3.0 nm, the turn-on voltage is reduced to 9.3 V, much lower than that mentioned above. The LiF layer thickness over 3.0 nm shifts the *I-V* and *L-V* curves back to the higher voltage region. EL emission could hardly be detected when the layer exceeded 5.0 nm. This indicates that whether the EL performance can be greatly

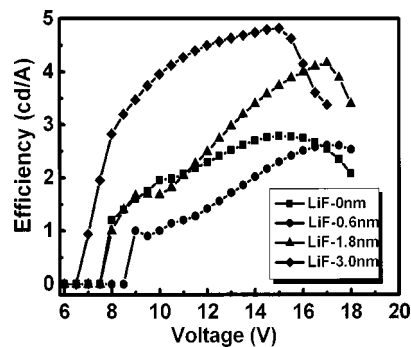


FIG. 2. Electroluminescent efficiency vs voltage curves with different LiF thicknesses: 0 nm (square), 0.6 nm (circle), 1.8 nm (triangle), 3.0 nm (diamond).

improved or not by using a Ag/LiF cathode structure strongly depends on the thickness of the LiF layer.

The curves of EL efficiency versus the bias voltage for the devices are shown in Fig. 2. The device without LiF exhibits poor EL performance, and the highest efficiency is only about 2.7 cd/A. Among the devices we fabricated, that with 3.0-nm-thick LiF gives the highest EL efficiency of 4.8 cd/A, which is comparable to that of the OLED with an Al/LiF cathode reported by Matsumura, Furukawa, and Jinde.⁸ It is interesting to note that the EL efficiency of the device with 0.6-nm-thick LiF is lower than that of the device without LiF. This is different from the case using Al/LiF as the cathode in OLEDs. The turn-on voltage as the function of LiF thickness is also plotted in Fig. 3. As shown in the figure, the turn-on voltages for the devices with LiF layer thicknesses of 0, 0.6, and 1.2 nm are 10.8, 11.3, and 11 V, respectively. This means that inserting a LiF layer thinner than 1.0 nm between Alq₃ and Ag would lead to turn-on voltage higher than that of the device without LiF. It is also evident that the device with 3.0-nm-thick LiF demonstrates the lowest turn-on voltage of 9.3 V. The optimal thickness of LiF layer for the OLEDs with the Ag/LiF cathodes is 3.0 nm. In contrast, the optimal thickness of LiF in small molecule OLEDs with Al cathode previously reported is around 0.5 nm.^{1,8} With Al used as the cathode, a LiF layer thinner than 1.0 nm would significantly improve the EL efficiency; when the LiF thickness is increased beyond 1.0 nm, the EL efficiency drops rapidly. In the experiments the EL performance of the OLEDs with Ag/LiF cathode structure can be signifi-

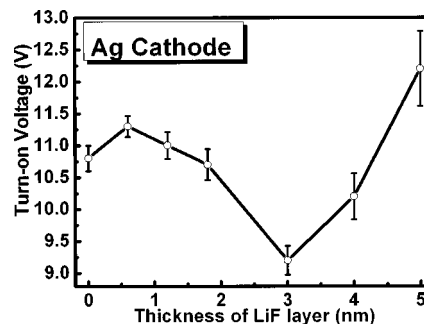


FIG. 3. Turn-on voltage of devices as a function of LiF thicknesses.

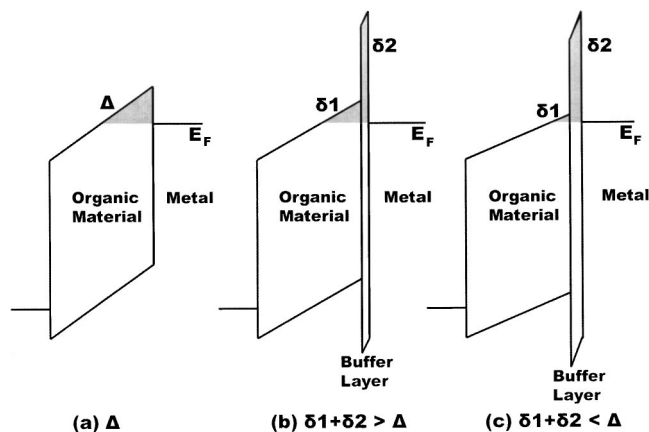


FIG. 4. Schematic of the tunneling model used to illustrate the electroluminescence characteristics of the devices with LiF thicknesses of: (a) 0 nm layer. (b) 0.6 nm and (c) 3.0 nm. Δ . The terms δ_1 and δ_2 represent the area of the tunneling barriers (shaded area) in the different cases.

cantly improved by using a 3.0-nm-thick buffer layer of LiF, much thicker than that for the Al/LiF cathode structure.

The performance enhancement in devices with Al/LiF/Alq₃ structure has been attributed to a chemical reaction involving LiF, Al, and Alq₃,⁶ and the thickness of the reacted layer is expected to be on the order of 1 nm or less. In the ternary system of Ag/LiF/Alq₃, it was indicated that the release of Li is thermodynamically inhibited.⁶ So, the enhancement of electron injection should be attributed to other mechanisms. Among the mechanisms proposed in the literature,^{9–13} the electron tunneling model could be tentatively applied to understand the LiF thickness dependence of the electron injection. Figure 4 is the schematic band diagram of the Ag/Alq₃ and Ag/LiF/Alq₃ tunneling junction, in which the tunneling barrier can be approximately represented by the shaded area.

If no buffer layer is included, the electron must tunnel through the triangle barrier, denoted by Δ , as shown in Fig. 4(a), in which the energy difference ΔE_{LF} between the lowest unoccupied molecular orbital and the cathode Fermi level (E_F) at the interface is unchangeable and independent of the applied voltage. In the presence of a buffer layer, the voltage drop across the layer raises the cathode E_F by the same amount and the subsequent barrier the electrons encounter, as shown by the shaded area in Figs. 4(b) and 4(c) can roughly

be regarded as two parts in series, the smaller triangle barrier (denoted by δ_1) at the organic side and the other barrier (denoted by δ_2) induced by the buffer layer.

We speculate that in the case of LiF layer thinner than 1.0 nm, the voltage drop across the buffer layer is small, and therefore, the decrease in barrier δ_1 is smaller than the additional barrier of δ_2 induced by the thinner LiF layer. Thus the total barrier ($\delta_1 + \delta_2$) [shown in Fig. 4(b)] might be larger. As a result, the devices show poorer EL performance. In the case of LiF layer with a proper thickness around 3.0 nm, the additional barrier of δ_2 induced by a thicker LiF layer is large compared with a thinner layer, but the barrier δ_1 at the organic side is dramatically reduced due to a larger voltage drop across the buffer layer. Hence, the total barrier potential ($\delta_1 + \delta_2$) [shown in Fig. 4(c)] becomes small and results in a great improvement of device performance. In the case of LiF layer thicker than 5.0 nm, the barrier induced by the LiF layer is very large. Further work aimed at a quantitative description of the phenomena is obviously needed. The above discussion is based on such a hypothesis that a complete LiF film is formed.

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