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Buffer-enhanced electron injection in organic light-emitting devices with copper cathode

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ABSTRACT

We explore in this work the use of Cu as a cathode material in organic light-emitting devices (OLEDs) and find a dual electron–injection enhancement mechanism derived from the LiF layer. Different from what observed previously in Ag- and Au-cathode devices, the LiF buffer layer in the Cu-cathode OLEDs starts to play its role in performance improvement when it is much thinner than 3 nm, the optimal value of buffer thickness, and in the case of optimal thickness, the device exhibits excellent performance comparable to conventional Al-cathode device. The phenomenon observed is ascribed to enhanced electron injection as a result of combined effect of interfacial reaction and tunneling barrier reduction mechanism: while chemical reaction plays a key role at the very beginning of interface formation, tunneling dominates in the subsequent stage leading to the tremendous improvement of the characteristics.

A metal with high work function is not considered as a suitable candidate for the cathode of organic light-emitting devices (OLEDs) usually. This is because the electrons injected from the cathode have to overcome a high potential barrier to get into the organic electron transport layer, resulting in poor electron injection. However, high work function metals have stable chemical property, which is quite beneficial to the lifetime of the devices. It was well recognized that the injection of electrons from an Al cathode could be significantly improved by using a LiF buffer layer inserted at the interface of organic and cathode, leading to a better performance and longer lifetime than that of the early $Mg_{0.9}Ag_{0.1}$ cathode [1]. The electron injection enhancement of the Al/LiF cathode is mainly ascribed to interfacial chemical reaction, as proved by photoelectron spectroscopy (PES) experiments [2–4]. But it was subsequently found that a 1 nm-thick LiF layer, as used in the case of Al cathode, had little or even negative effect on injection enhancement for cathodes made of other metals [5]. It implied that chemical reaction was not universally applicable to LiF-buffered cathodes in OLEDs. In 2004, Wang et al. [6] found that the electron injection and resulting performance of the device with Ag cathode could be quite enhanced when the thickness of LiF layer increased up to 3 nm, indicating the presence of a very different mechanism which was considered to be tunneling. More recently, it was found that the same mechanism could be applied to Au-cathode OLEDs [7]. The two mechanisms are sharply different from each other and just occur solely in previous researches. In this work, we study the role of LiF buffer in Cu-cathode OLEDs. Cu is a more widely used electrode material relative to Ag and Au in electronic industry. It is found that the Cu/LiF cathode behaves in a different way than neither the Ag/LiF and Au/LiF cathodes nor the Al/LiF cathode: no matter the LiF buffer is much thinner than optimal thickness or at it, enhanced electron injection can always be observed. A reaction-and-tunneling-combined mechanism is thus proposed to explain the phenomenon observed.

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The experiments were performed in a clean room. The devices had sandwiched structure. Transparent ITO (indium tin oxide) glasses, with sheet resistance of 15 Ω/square, were used as substrate and anode, on which N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and tris-(8-hydroxyquinoline) aluminum (Alq_3) were deposited orderly as hole-transport layer and electron-transport/luminescent layer separately. Then LiF layers with different thickness were deposited as buffer layer. A thin Cu layer was finally deposited on the top to act as cathode of the device. The ITO glass substrate was cleaned with lotion (Formula 224) and ultrapure water and pretreated by ultraviolet-ozone to enhance the hole injection. All the functional materials and metal cathode were deposited by thermal evaporation in a preparation chamber with base pressure of 1×10^{-5} Pa. Four samples could be fabricated at one time, and masks were used to ensure that the organic layers and cathode were exactly identical while the LiF layer had different thicknesses for the four devices. The deposition rate of Cu cathode was ca 2 Å/s. The purity of all the materials was higher than 99% and all deposition rates were detected with a quartz crystal oscillator. The current–voltage and luminance–voltage characteristics were measured by Keithley 236 source measure unit, Keithley 2000-20 multimeter and ST-86LA luminance meter in atmosphere environment at room temperature.

The solid circles in Fig. 1 represent the electrical and luminescence characteristics of the four devices fabricated in one batch, with the structure of ITO\NPB (40 nm)\Alq_3 (80 nm)\LiF (x nm)\Cu (80 nm). Here x varies from 0 nm to 3 nm. One can see that the performance of the buffer-free ($x = 0$) device is poor. The current density and luminescence are 78 mA/cm^2 and 385 cd/m^2, respectively, at the bias voltage of 18 V. And the resulting current efficiency is as low as 0.48 cd/A. All the characteristic parameters are far from those of conventional device. After inserting a 1 nm-thick LiF layer between Alq_3 and Cu cathode, the current density and luminescence are both increased, reaching 122 mA/cm^2 and nearly 1700 cd/m^2, respectively. Accordingly, the current efficiency reaches its maximum of 1.4 cd/A. That is an appreciable improvement in electron injection for the Cu cathode. This variation, induced by the insertion of a 1 nm-thick LiF layer, is different from that of the devices with Ag, Au and some other metallic cathodes [5–7] after the same processing, where 1 nm LiF layer could just have negative effect on electron injection. The performance of the device keeps on improving as the LiF buffer layer thickness increases. A 2 nm-thick LiF layer can raise the current density to 222 mA/cm^2 and luminance to 5700 cd/m^2 when the device operates at the driving voltage of 18 V. This is already an overloaded working voltage and the luminance trends to decay there, as one can also see in the current efficiency curve. The efficiency reaches its maximum at 3 cd/A and decays thereafter for higher currents. When the LiF thickness increases to 3 nm, the device reaches the best performance in our experiment. The turn-on voltage decreases sharply, indicating an excellent electron injection and carrier balance in this case. The current density reaches 231 mA/cm^2 under a lower voltage of 16 V for the sake of avoiding decay,

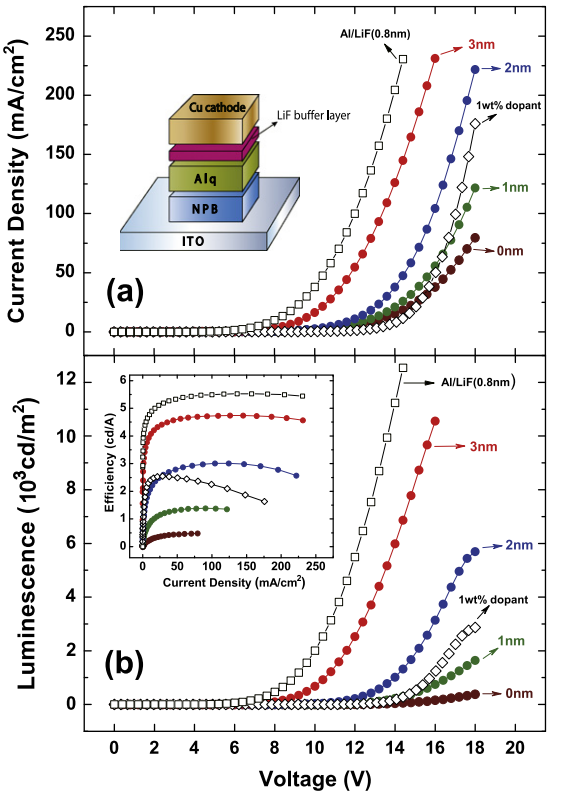

Fig. 1. The (a) electrical and (b) luminescence characteristics of the devices with different LiF buffer layer thickness from 0 nm to 3 nm. The insets show the device structure and the current efficiency, respectively. The performances of the devices with LiF-doped Cu cathode and conventional Al/LiF (0.8 nm) cathode are also shown for comparison.

which is still larger than that of 2 nm-LiF device under 18 V. The luminance reaches almost 11,000 cd/m^2 at 16 V and the maximum current efficiency reaches 4.8 cd/A. The device with the commonly-used Al/LiF (0.8 nm) cathode is also fabricated for reference, which is denoted by the hollow squares. With the modification of 3 nm LiF buffer layer, the performance of Cu-cathode OLED is not very far from that of the conventional Al-cathode device. However, the driving voltage is somewhat higher, which is considered to arise from the higher impedance of the device derived from the much thicker insulative LiF layer. The LiF buffer layer of 4 nm thickness leads to a start of decline for both current and luminance, which is not shown here. When the LiF layer is thickened to 5 nm, not only the current and luminance of the device decay further, but also the stability degrades significantly. The device with a 6 nm-thick LiF layer has almost no luminance, and the current density is the lowest too. Further thicker LiF layers are not adopted for being reasonably predicted to have only negative effect and make the device performance worse.

To show the results more comprehensively and explicitly, we plot in Fig. 2a the effect of LiF buffer layer as the function of LiF thickness, from which it can be seen that both the current and the luminance of the device increase monotonously before the optimal thickness (3 nm) and decline after that. It is intriguing to compare the evolution of