

Alq₃-based organic light-emitting devices with Al/fluoride cathode: Performance enhancement and interface electronic structures

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The device characteristics and the interface electronic structures of organic light-emitting devices based on *tris*-(8-hydroxyquinoline)aluminum were investigated with Al/CaF₂, Al/LiF, and Al-only cathodes. Similar to the Al/LiF cathode, the Al/CaF₂ cathode greatly improved the performance of the device over Al-only cathode. However, a photoelectron spectroscopy study revealed that despite the performance improvement, the evolution of the new peaks during Al/CaF₂ cathode formation closely resembled those of the Al-only cathode rather than the Al/LiF cathode.

Organic light emitting devices (OLEDs) have been attracting considerable attention because of their application to flat panel display technology. *Tris*-(8-hydroxyquinoline)aluminum (Alq₃) is one of the most widely used materials for OLEDs due to its excellent stability and luminescent properties. [1, 2] A typical OLED consists of a low work function metal (LWFM) as a cathode and a high work function indium-tin-oxide (ITO) as a transparent anode. It has recently been reported that the performance of OLED can be greatly improved by introducing interlayers between the emitting layer and the cathode. [3-7] The mechanism behind the improvement with the interlayer has not been fully understood and became a subject of debate. [8, 9]

X-ray and UV photoelectron spectroscopy [(XPS) and (UPS), respectively] studies have shown that gap states are formed upon deposition of LWFMs on Alq₃ and Al on LiF/Alq₃. [3, 10-15] Concurrently, a shoulder peak at the lower binding energy (BE) side of the N 1s core level peak was observed. These common features of electronic structures in two different systems are presented as the evidence for identical underlying physical processes, which is charge transfer from LWFM to Alq₃. This suggests, in the case of LiF, dissociation of the fluoride into Li and F. However, we recently reported that the interface electronic structure of Al/MgF₂/Alq₃ showed different trend from those found in Al/LiF/Alq₃ and LWFM/Alq₃, [8] in which we suggested that the formation of gap states may not be directly related to the improved device performance. In this letter, we show that while the performance of OLEDs with Al/CaF₂ cathode is greatly improved over the one with Al-only cathode, the interface electronic structure of Al/CaF₂/Alq₃ is rather different

from that of Al/LiF/Alq₃ and resembles that of Al/Alq₃.

The structure of the OLEDs was Al(100)/fluoride/Alq₃(60)/TPD(60)/ITO(60). Layer thicknesses indicated are in nm. They were fabricated under the vacuum of 3×10^{-8} Torr and the active area was set to 2×2 mm². The current-voltage (*I-V*) and luminance-voltage (*L-V*) characteristics were measured in air under forward bias using a Keithley 236 source-measure unit and a calibrated Minolta CS1000 optometer. The XPS and UPS experiments were carried out in an ultrahigh vacuum chamber that is connected to a preparation chamber where all deposition processes took place. Spectra were recorded on VG ESCALAB 220 using a He I (21.2 eV) source for UPS and a Mg K_α (1253.6 eV) source for XPS. The base pressure of the preparation chamber and the analysis chamber were 7×10^{-9} and 5×10^{-10} Torr, respectively. The UPS spectra were recorded with a bias of -20 V. Energy resolutions were approximately 0.1 eV and 1.0 eV for UPS and XPS, respectively. The deposition rate was carefully monitored by crystal quartz microbalance and was typically 0.1 nm/min. Ten nm-thick Alq₃ film was initially deposited on indium-tin oxide as the starting surface for the XPS and UPS study.

In Fig. 1 we show *I-V* and *L-V* curves of four devices with different cathode types including Al-only, Al/CaF₂(2 nm), Al/LiF(1 nm), and Al/LiF(2 nm). The inset of the Fig. 1(b) shows corresponding external quantum efficiencies (EQE). The performance of devices with Al/LiF cathodes were also shown for comparison, which is similar to the one reported previously. [4] It is clear that the performance of Al/CaF₂ cathode was greatly improved over Al-only cathode in terms of turn-on voltage and quantum efficiency. In fact, the maximum EQE of Al/CaF₂(2 nm) cathode was almost 40 times better (0.037 % vs. 1.3 %) than the Al-only cathode. Compared with Al/LiF cathode, the EQE of Al/CaF₂(2 nm)

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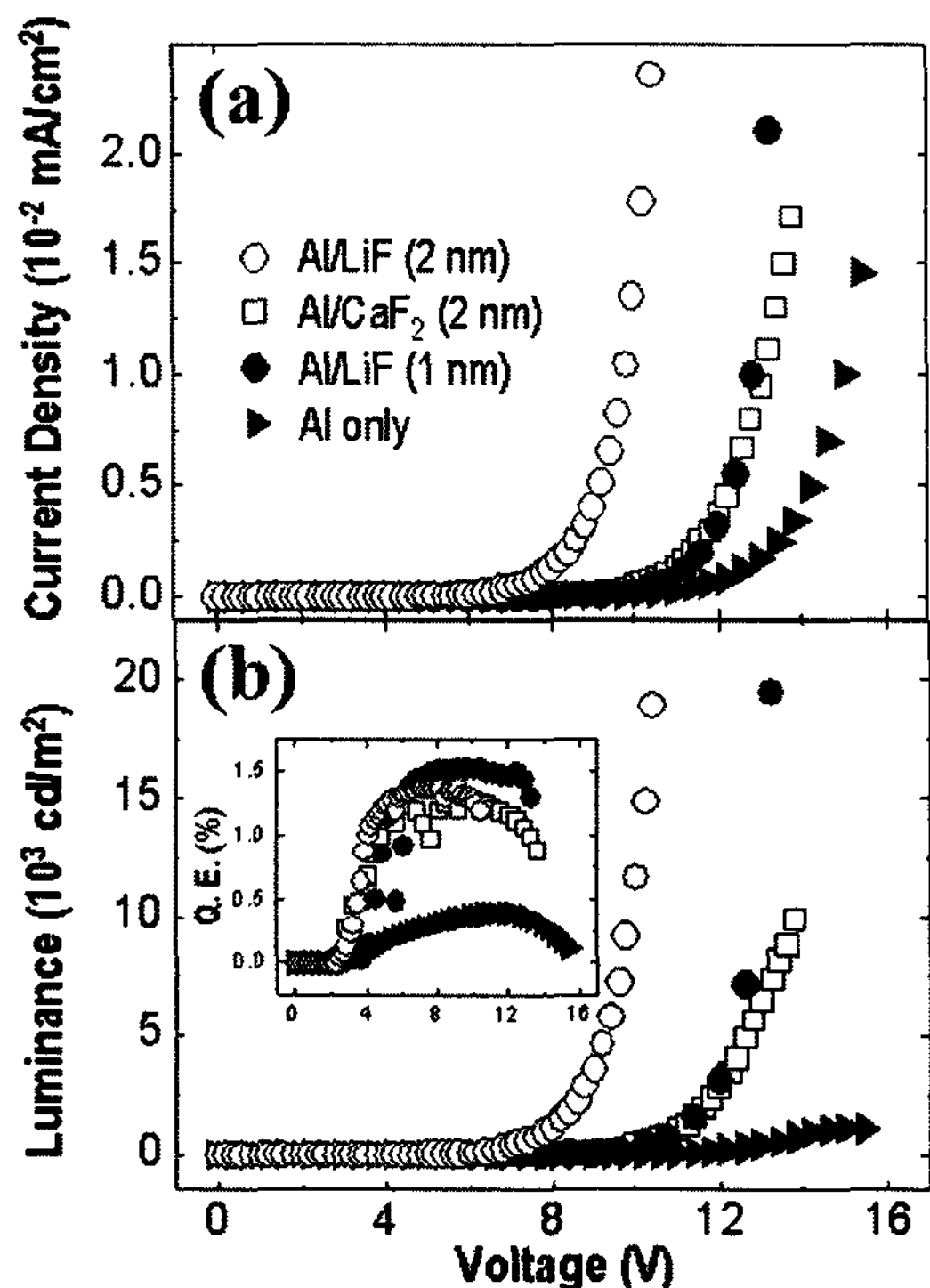


FIG. 1: (a) Current-voltage (I - V) and (b) luminance-voltage (L - V) curves of the devices with Al/LiF/Alq₃, Al/CaF₂/Alq₃, and Al/Alq₃ interfaces. Inset of (b) shows the external quantum efficiency (EQE) of the same devices.

and Al/LiF(2 nm) cathodes are similar and turn-on voltage of Al/CaF₂(2 nm) and Al/LiF(1 nm) cathodes are similar. The best EQE and the lowest turn-on voltage were observed in Al/LiF(1 nm) and Al/LiF(2 nm) cathodes, respectively. From these we conclude that although the performance Al/CaF₂(2 nm) cathode is certainly not better than Al/LiF cathodes but it is pretty close.

Figure 2 shows the evolution of valence band UPS spectra while three different types of cathodes were being deposited on Alq₃. The energy reference in these spectra is Fermi level, E_F . The highest occupied molecular orbital (HOMO) peak of Alq₃ initially starts at around 2.5 eV and shifts toward the high BE side upon overlayer deposition. For LiF and CaF₂ deposition on Alq₃ the amount of shift was about 1.5 eV at the coverage of 0.5 nm, and additional deposition of Al on the fluoride did not significantly shift the peaks. The peak shift was also evident for Al deposition on Alq₃, but the amount of shift, about 0.5 eV, was much smaller than the fluoride cases. In all cases the deposition of Al caused an extra peak to appear, which is the sign of gap state formation. Even for the Al-only cathode, the gap state peak was clearly observed as seen in Fig. 2(b), [15] which is in contrast with what was previously reported.[6] The gap state peak is

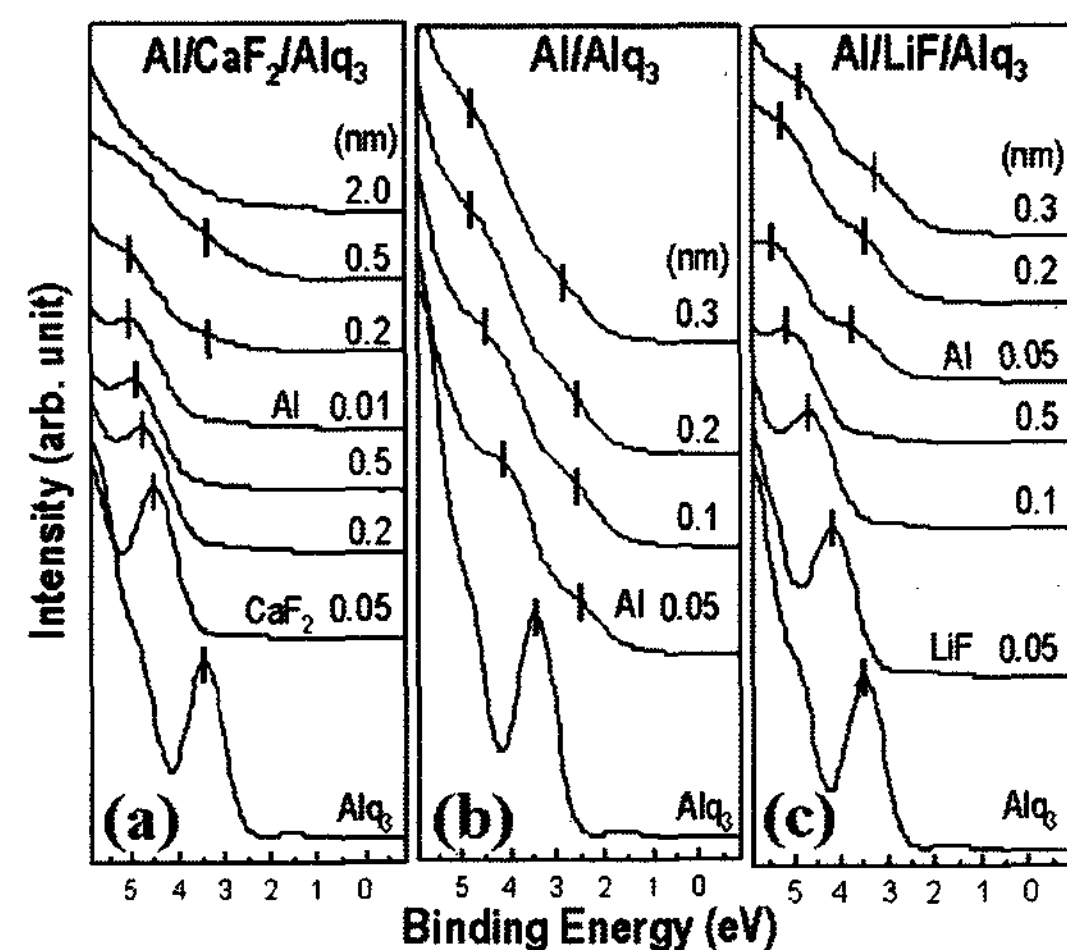


FIG. 2: (a) The evolution of the valence band spectra for Al/CaF₂/Alq₃ interface with increasing CaF₂ and Al coverage. Similar spectra for Al-only (b) and Al/LiF (c) cathodes are also shown. The vertical bars indicate HOMO position and gap states.

strongest in Al/LiF and weakest in Al/CaF₂. It is noteworthy that the deposition of Al and formation of gap states for CaF₂/Alq₃ and LiF/Alq₃ did not significantly change the HOMO position. This is in sharp contrast with what was observed for direct metal deposition on Alq₃ including Al.[6, 15]

It is well known from the studies of metal deposition on Alq₃ that the formation of gap states in valence region accompanies the appearance of shoulder peak in low BE side of the N 1s core level peak of Alq₃ due to a charge transfer from the metal atoms. The evolution of N 1s core level peak for three different types of cathodes is shown in Fig. 3. The deposition of both CaF₂ on Alq₃ and LiF on Alq₃ did not seem to cause any significant change to the N 1s peak except for the slight peak position shift and broadening. The deposition of Al, regardless it is on CaF₂/Alq₃, LiF/Alq₃, or pristine Alq₃, caused shoulder peak formation. [6, 15] Although the data is a little bit noisy, it is easy to see that the shoulder peak is strongest in Al/LiF/Alq₃. Its intensity is similar for Al/CaF₂/Alq₃ and Al/Alq₃. This is quite similar to the case of relative gap state peak intensity in the valence region spectra.

From the valence and core level electronic structures probed by UPS and XPS, it is clear that the similarity between Al/LiF cathode and Al/CaF₂ cathode is peak shift behavior when LiF or CaF₂ was deposited on Alq₃. The subsequent changes due to Al deposition including the gap state formation and the appearance of N 1s shoulder peak show very different trend for the two cathodes that exhibited common OLED performance improvements. As we have reported previously,[8] the elec-

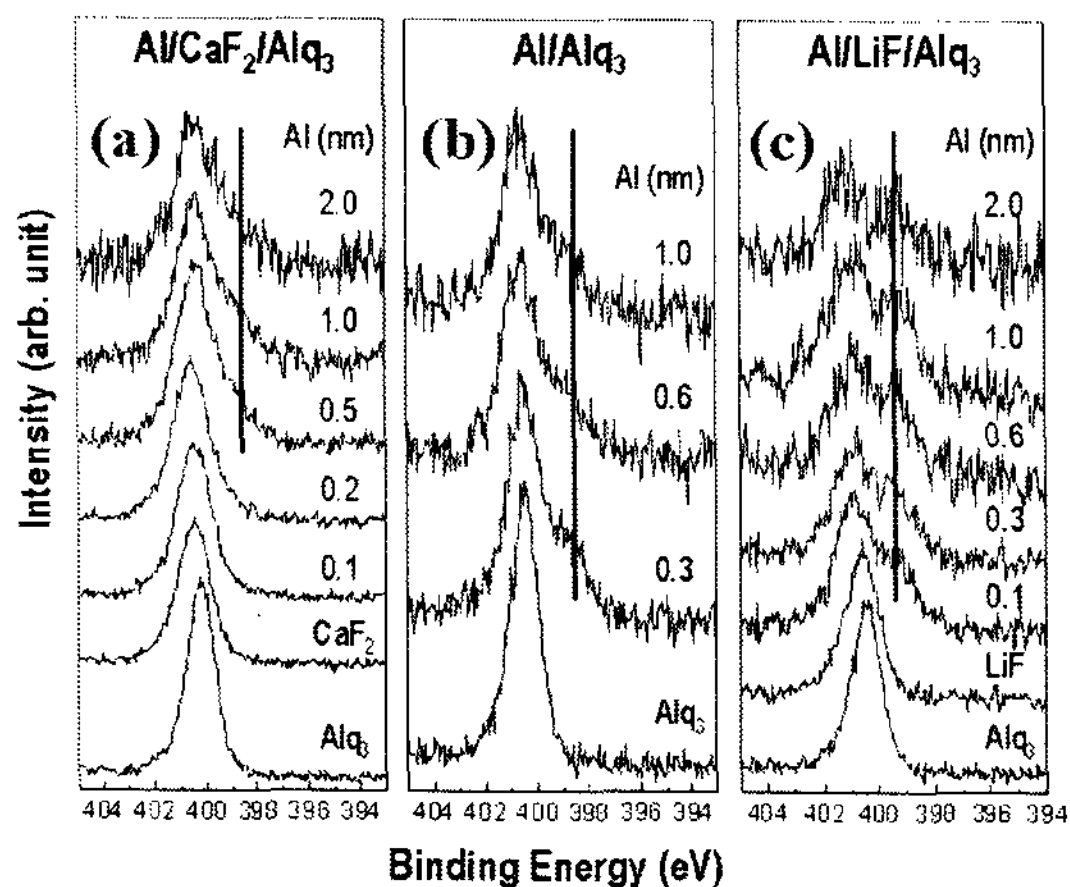


FIG. 3: (a) The evolution of N 1s XPS core level spectra of Al/CaF₂/Alq₃ interface. (b) Similar evolution of Al/Alq₃ interface and (c) Al/LiF/Alq₃ interface. The vertical lines indicate shoulder peaks created upon Al deposition

tronic structure of Al/MgF₂/Alq₃ interface is also different from that of Al/LiF/Alq₃, while exhibiting common improved OLED performance.[16]

These findings suggest that not the formation of new peaks or states but the valence band shift itself is related with the improved OLED performance in Al/CaF₂ cathode. If the valence peak shift upon CaF₂ deposition represents rigid shift of all the valence levels including the lowest unoccupied molecular orbital (LUMO), it is easy to see that the LUMO pull-down relative to E_F and resultant lower electron injection barrier is the main reason for the improved device performance.

The origin of the gap states and N 1s shoulder peak observed in Al/CaF₂/Alq₃ is not clear at this stage. It might be due to the charge transfer from Ca after CaF₂ was dissociated.[3, 6] Other possibility is that the Al deposited on CaF₂/Alq₃ might still find the bare Alq₃ surface and partially form Al/Alq₃ interface. This is quite probable because the thin (0.5 nm) layer of CaF₂ may not completely cover the Alq₃ surface. Then the Al/CaF₂/Alq₃ cathode can have mixed Al/Alq₃ and Al/CaF₂/Alq₃ interfaces, and the former can give rise to gap states and N 1s shoulder peak as seen in Figs. 2(b) and 3(b).

The remaining question is the origin of the peak shift due the CaF₂ deposition. Since the peak shift occurred before metal deposition, the gap states induced by metal cannot be responsible for the shift. The interface dipole layer formation was suggested for the origin of the work function change. [4, 17] But the dipole layer should not shift the HOMO level, which is referenced to the Fermi

level. We speculate that the pinning of the Fermi level due to some kind of chemical reaction between fluoride and Alq₃ might be the origin of the observed peak shifts.

In summary, we have shown that the Al/CaF₂ cathode deposited on Alq₃ greatly improved the OLED performance over Al-only cathode, but the interface electronic structures probed by UPS and XPS are not very different from each other except for the amount of peak shift. These results suggest that the improved device performance comes from HOMO level shift that occurs as soon as the fluoride was deposited, and not closely related with new peak formations caused by subsequent Al deposition.

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