Alq_3-based Organic Light-Emitting Devices with Al/NaF cathodes: Performance Enhancement and Interface Electronic Structures

Y. Park[1], J. Lee[2], D. Y. Kim[3], H. Y. Chu[4], H. Lee[4], and L.-M. Do[4]

[1]Nano-Surface Group, KRISS, Taejon 305-600, Korea

[2]SAIT AE Center, Yongin 440-600 Korea

[3]Chemistry and Physics Division, Hallym University, Chunchon 200-702, Korea

[4]Basic Research Laboratory, ETRI, Taejon 305-600, Korea

Phone : +82-42-868-5397 , E-mail : park@kriss.re.kr

Abstract

The device characteristics and the interface electronic structures of organic light-emitting devices based on /tris-(8-hydroxyquinoline)aluminum (Alq_3) were investigated with Al/NaF cathode. The Al/NaF cathode greatly improved the performance of the device over the Al-only cathode. A series of photoelectron spectroscopy studies on cathode structures including Al/LiF and Al/CaF_2 revealed that the performance enhancement originated mainly from the HOMO peak shift upon the fluoride deposition rather than the formation of the gap states

1. Introduction

Since the organic light-emitting devices (OLEDs) have been attracting considerable attention for their applications on flat panel display, many efforts have been made to improve the performance of OLEDs. A typical OLED consists of a low work function metal as the cathode and a high work function indium tin oxide (ITO) coated glass as a transparent anode with *tris*-(8-hydroxyquinoline)aluminum (Alq_3) as an emitting material layer. One of the marked OLED performance improvements has been achieved by employing the insulating thin layer between the metal cathode and the emitting material layer.[1–5]

In recent photoelectron spectroscopy studies, it was observed that the deposition of interlayer yields the valence band shift including the highest occupied molecular orbital (HOMO) even before the aluminum (Al) deposition.[2,3,6–8] With the deposition of Al on LiF/Alq_3 , the gap states were formed and a shoulder peak at the lower binding energy (BE) side of N 1*s* core level developed. These features of electronic structures are presented as the evidence for identical underlying physical process, which is charge transfer from metal to Alq_3. The gap states formation had been thought as a major factor of the enhancement of OLED performance.

However, we have suggested that the improved performance comes from the HOMO level shift resulting from the fluoride deposition in our previous photoemission studies on Al/CaF2/Alq_3, Al/LiF/Alq_3, Al/Alq_3, and Al/MgF_2/Alq_3 interfaces.[7,8] Tunneling through a metal fluoride layer was proposed to explain the enhancement of OLED performance.[5] The formation of a dipole layer across the interface leading to a vacuum level offset between the organic layer and the Al cathode was initially proposed by Shaheen *et al.*,[9] and recently Brabec *et al.* also suggested it as a mechanism for the enhancement of the performance. [10] Later, dissociation of the LiF and doping mechanism of the organic layer was proposed by Le *et al.*[3] In this paper, we show that the performance of OLEDs with the Al/NaF cathode is greatly improved over the one with the Al-only cathode and is as efficient as the established Al/LiF cathode. Photoelectron spectroscopy studies revealed that the intensity of the gap states and the amount of the valence band shift at Al/NaF/Alq_3 interface surpassed those of Al/LiF/Alq_3 interface, suggesting that the observed performance improvement is directly related with these features.

2. Experimental

The structure of the OLED was set to Al(100 nm)/metal fluoride interlayer/Alq_3(60 nm)/TPD(60 nm)/ITO(60 nm). The active area was 2X2 mm^2. The current–voltage ($I-V$) and the luminance–voltage ($L-V$) characteristics were measured in air under forward bias using a Keithley 236 sourcemeasure unit with a calibrated Minolta CS1000 optometer. The XPS and UPS experiments were carried out in an ultrahigh vacuum analysis chamber, which was connected to a

preparation chamber where all deposition processes took place *in situ*. Spectra were recorded on VG ESCALAB 220 using a He I (21.2 eV) radiation source for UPS and a Mg K a (1253.6 eV) radiation for XPS. UPS spectra were recorded with a bias of -10 V on the sample for the observation of the low energy cutoff. Energy resolutions were approximately 0.1 and 1.0 eV for UPS and XPS, respectively. The deposition rate was 0.1 nm/min.

3. Results and discussion

Figure 1 shows the $I-V$ and $L-V$ characteristics of six devices with different cathode and different interlayer thickness, Al-only, Al/LiF(1 nm), Al/NaF(0.5 nm), Al/NaF(1 nm), Al/NaF(1.5 nm), and Al/NaF(2.0 nm). The inset of Fig. 1(b) shows corresponding external quantum efficiencies (EQEs). The Al/LiF(1 nm) device was examined along with Al/NaF devices, as it showed the best performance among Al/LiF devices. It is clear that the performance of Al/NaF device was greatly improved over Al-only device in terms of turn-on-voltage and EQE. The performance of Al/NaF device is comparable (NaF 1 nm) or slightly better (NaF 1.5 nm) than the best Al/LiF device. It is noteworthy that the OLED performance depends upon the thickness of NaF. The performance drops in Al/NaF (2 nm) device, which is similar to that of Al/NaF (0.5 nm) device. When the NaF layer is too thin (0.5 nm) it cannot cover the entire Alq3 surface and the deposition of Al creates inefficient direct Al/Alq3 interface. This is why Al/NaF(0.5 nm) device showed poorer performance than Al/NaF(1 nm) device although the electronic structure change relevant to the performance improvement already took place when 0.5 nm of NaF was deposited as we shall see shortly. On the other hand, when NaF layer is too thick (2 nm), the insulating nature of the NaF layer acts itself as an electron injection barrier, which also results in degraded performance.

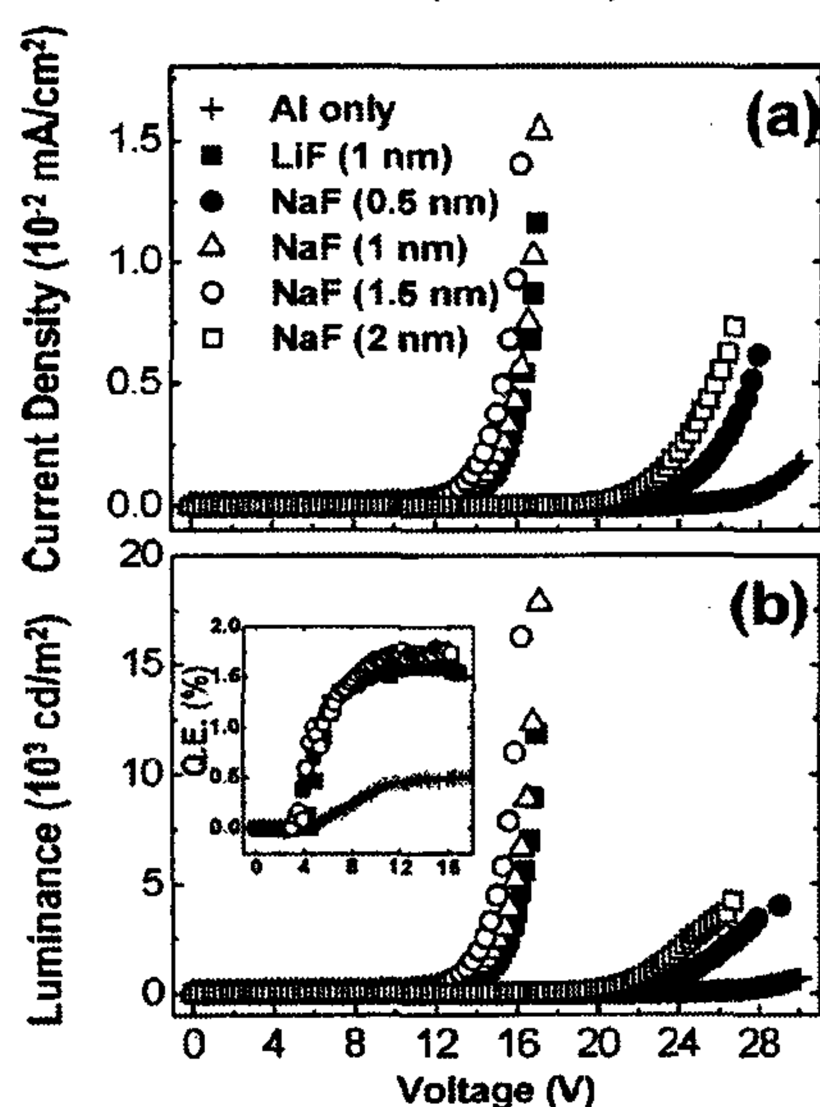

Figure 1. (a) *I-V* and (b) *L-V* characteristics of OLED with Al/Alq_3, Al/LiF/Alq_3, and Al/NaF/Alq_3 interfaces. The inset of (b) shows the external quantum efficiencies of the OLEDs.

Figure 2 shows the evolution of valence band UPS spectra while two different types of cathodes were being deposited on Alq_3. The BE in Fig. 2 is relative to the Fermi level, E_F. A pristine Alq_3 layer is shown at the bottom of the figure. The onset of the peak at the lowest binding energy is referred to as the HOMO level and is attributed to the orbital located on the phenoxide side of the quinolate ligand. The HOMO peak of Alq_3 shifts towards the high BE side upon overlayer deposition. For LiF and NaF deposition on Alq_3, the amount of shift was about 1.5 and 1.9 eV, respectively, at the coverage of 0.5 nm. This is similar with the cases of MgF_2 and CaF_2 deposition on Alq_3 where significant valence band shift occurred when metal fluoride layer was deposited.[7,8] As seen in

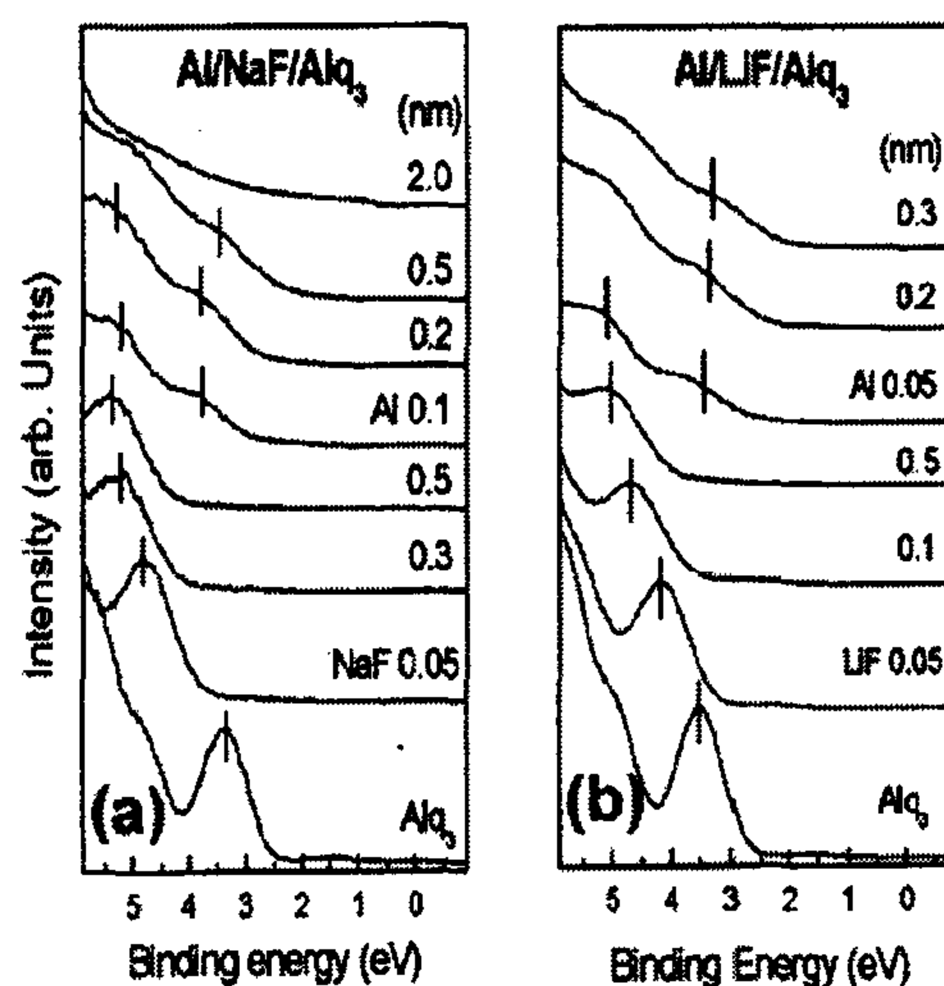

Figure 2. (a) The evolution of the valence band spectra for Al/NaF/Alq3 interface with increasing NaF and Al coverage. (b) Similar spectra but for LiF in place of NaF. The vertical bars indicate the HOMO position and the formation of gap states.

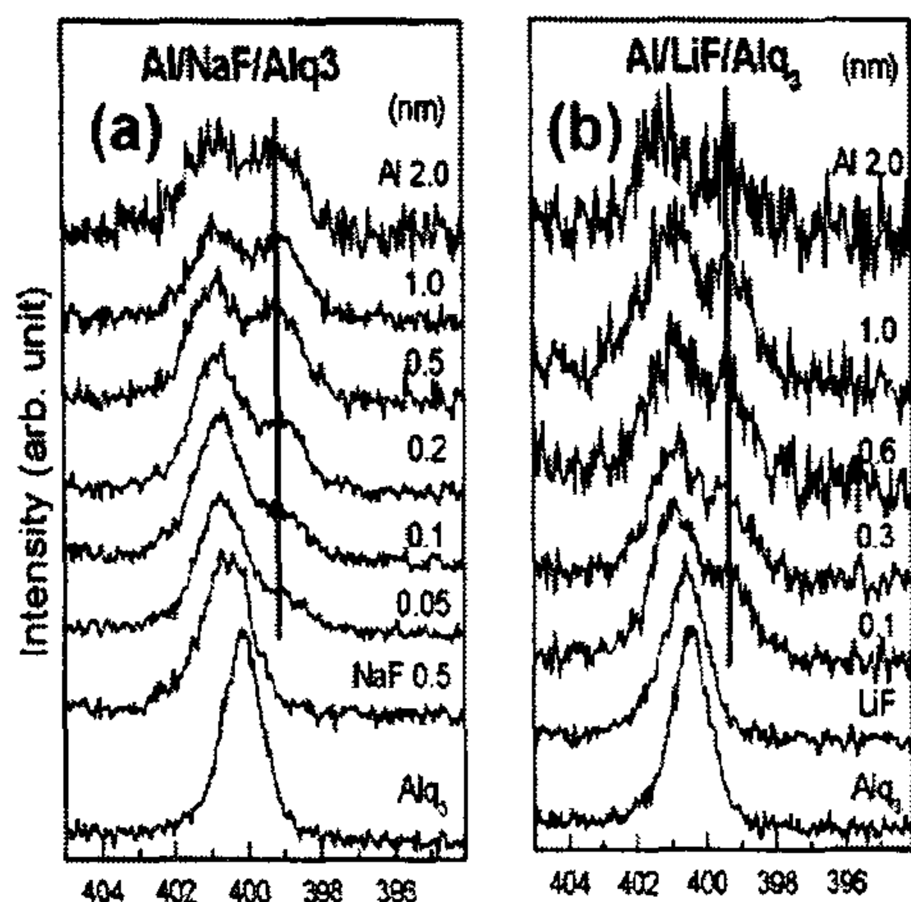

Figure 3. (a) The evolution of XPS core level peak of N 1*s* peak with NaF and Al deposition. The binding energy is relative to the Fermi level. (b)Similar evolution of Al/LiF/Alq3 interface. The vertical lines indicate the evolving extra peaks resulting from Al.

Fig. 2, the deposition of Al on the fluoride-covered Alq_3 causes no significant peak shift but forms prominent gap states, which is the only difference with MgF_2 and CaF_2 cases, where the intensity of the gap states was very weak. The evolution of the N 1*s* core level peak for Al/NaF and Al/LiF cathodes are shown in Fig. 3. The appearance of N 1*s* shoulder peak on the lower BE side is attributed to a charge transfer from the metal atoms. In both systems, the evolution of the shoulder peaks shows similar trend. The intensity of the shoulder peaks is also very similar, indicating that the charge transfer from the metal cathode to Alq_3 is comparable in these cases. If the HOMO level shift by metal fluorides layer deposition represents a rigid shift of all the valence levels including the lowest unoccupied molecular orbital (LUMO), then the LUMO pull-down relative to E_F and resultant lower electron injection barrier should be the main reason for the improved OLED performance. Therefore, these results clearly support that the HOMO level shift is directly related with the OLED performance improvement. However, what is not clear is how the deposition of Al layer alters this scenario. In NaF (and LiF) case, the Al deposition forms strong gap state as a result of charge transfer, which might come either from Al or Na, whereas in MgF_2 and CaF_2 cases, there seems to be no significant charge transfer. Considering that device performance was improved in all cases, we suggest that the HOMO level shift is correlated with the OLED performance improvement.

4. Conclusion

In summary, Al/NaF(1.5 nm) cathode in Alq_3-based OLED exhibited highly improved performance, which is comparable to the best device with Al/LiF cathode. The XPS and UPS results show that the amount of valence band shift resulting from the NaF deposition surpasses that of the LiF deposition. The Al deposition causes gap state formation and a shoulder in N 1*s* core level peak similar to LiF case. Device performance results indicate that the valence band shift is correlated with the enhancement of the OLED performances.

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