

Photoelectron Spectroscopy Study of the Electronic Structures of Al/MgF₂/tris-(8-hydroxyquinoline)aluminum Interfaces

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(Received ; accepted November 19, 2001; accepted March 13, 2002))

We have studied the electronic structures of Al/MgF₂/tris-(8-hydroxyquinoline)aluminum (Alq₃) interface using UV and X-ray photoelectron spectroscopy (UPS & XPS). The UPS revealed that the valence peak shift occurred with MgF₂ deposition before Al was deposited and was independent of the gap state formation. The XPS core level peaks indicated that the MgF₂ strongly interacted with Al and O atoms in Alq₃ even before Al was deposited, and the deposition of Al caused slight change to the N 1s core level peak. These results indicate that the interaction mechanism in Al/ MgF₂/Alq₃ is different from those found in Al/LiF/ Alq₃ and other metal/Alq₃.

Since the report of electroluminescence in tris-(8-hydroxyquinoline)aluminum (Alq₃)-based organic light-emitting devices (OLED),[1] related materials and devices have been attracting much attention due to the application in flat panel displays. A typical OLED is composed of a transparent bottom electrode, organic active layers and a top metallic electrode. The charge carriers that form emissive species in the organic layers are injected through the energy barriers at the electrode-organic interfaces. It was recently found that great improvements in OLED performance could be achieved when a thin insulating layer is inserted between the organic layer and Al electrode.[2-4] These insulators include LiF, MgF₂, MgO, and Al oxides. However, the mechanism with which the insulating layer improves the OLED performance is not clear, as these materials are chemically stable and the optimum thickness for the improved performance is often too thin to form a continuous layer.

Previous valence band studies using

ultraviolet photoelectron spectroscopy (UPS) have shown that gap states are formed upon deposition of low work function metals (LWFM) on Alq₃. [5-9] It is believed that the LWFM atoms donate charges to Alq₃ molecules and create the gap states. Later, it was reported that the deposition of Al on LiF/Alq₃ also forms gap states.[10] This similarity led to a LiF dissociation scenario for Al/LiF/Alq₃ system in which Li atoms, liberated by LiF dissociation, donate charges and create the gap states.[10] In addition, both LWFM/ Alq₃ system and Al/LiF/Alq₃ system exhibited a shoulder peak in the lower binding energy (BE) side of the N 1s peak when studied with X-ray photoelectron spectroscopy (XPS). In both systems the appearance of shoulder peak coincides with the formation of the gap states in valence band. The Al/MgF₂/ Alq₃ interface has been considered similar to Al/LiF/Alq₃. However, we report in this paper that the interface electronic structures of Al/ MgF₂/Alq₃ observed with UPS and XPS are different from those of Al/LiF/ Alq₃ and

LWFM/Alq₃.

The XPS and UPS experiments were carried out in an ultrahigh vacuum (UHV) analysis chamber that is connected to a preparation chamber, in which all the depositions were performed. The base pressures of the preparation chamber and the analysis chamber were 5×10^{-9} and 5×10^{-11} Torr, respectively. The deposition was monitored by quartz crystal microbalance and the typical rate was 0.1 - 0.2 nm/min. The UPS measurements were performed with a He I (21.2 eV) gas discharge lamp and the XPS measurements with Mg *K_α* X-ray source (1253.6 eV) utilizing a modified VG ESCALAB 220 electron energy analyzer. Sample was biased by about 20 V when UPS measurements were performed. Overall energy resolutions were about 0.1 eV and 1.0 eV for UPS and XPS, respectively.

About 10 nm thick Alq₃ film was initially deposited on indium-tin oxide (ITO) glass as the starting surface. Figure 1(a) is a series of valence band spectra of MgF₂/Alq₃ with increasing MgF₂ layer thickness. The BE in Fig. 1 is relative to the vacuum level and the position of the Fermi level (E_F) is indicated with a vertical bar. The bottom spectrum is for pristine Alq₃, which is similar to those found in the literature.[11,12] The onset of the first peak at low BE is referred to as the highest occupied molecular orbital (HOMO) and its position is 5.8 eV (2.2 eV below E_F) in good agreement with the reported value. [5,7,13] With the deposition of MgF₂, the E_F shifted toward lower BE direction and the peaks were gradually broadened. The amount of shift is about 1.7 eV at MgF₂ coverage of 0.5 nm. The evolution of valence region spectra with Al deposition on the MgF₂ (0.5 nm)/Alq₃ (10 nm) is shown in Fig. 1(b). The formation of gap states indicated with an arrow is clearly observed, although the intensity is weak. The deposition of Al did not further shift the E_F positions. Only when the Fermi edge due to the metallic Al was visible did the E_F move toward

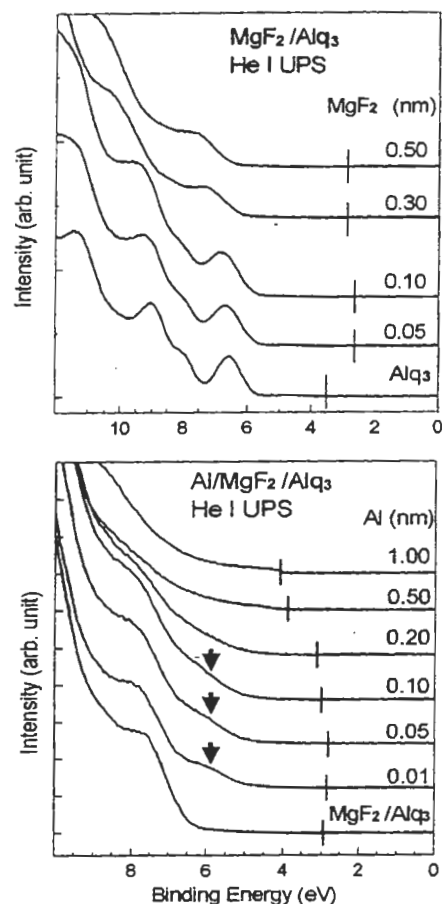


Fig. 1 (a) The evolution of the valence band spectra for MgF₂/Alq₃ with increasing MgF₂ coverage. The binding energy is relative to the vacuum level. The Fermi level is indicated with a vertical bar in each spectrum. (b) Similar spectra of Al deposition on MgF₂/Alq₃. The gap states indicated with arrows are clearly observed.

the high BE. Recent studies on Al/LiF/Alq₃ interface reported similar gap state formation and peaks shift. [10,14] However, the peak shift occurs only after Al deposition in one of the reported results.[10]

Figure 2(a) shows the evolution of Al 2*p* core level peak upon deposition of MgF₂ and Al. The BE in Fig. 2 is relative to E_F . The single peak at 74.4 eV in the bottom spectrum is attributed to Al atoms in pristine Alq₃. The deposition of 0.5 nm MgF₂ produced an extra peak in the higher BE side at about 1.7 eV from

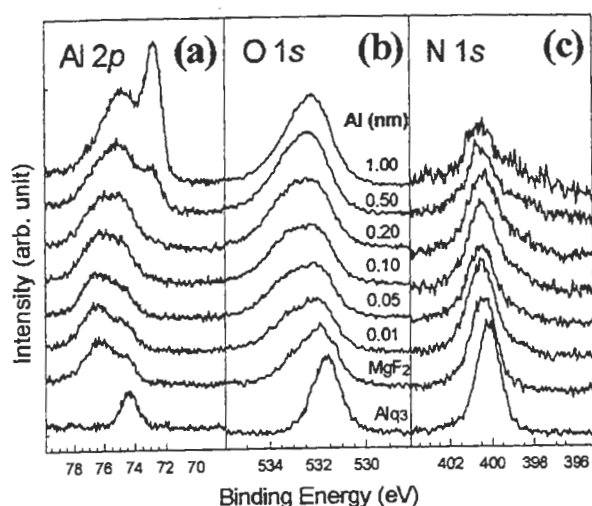


Fig. 2 (a) The evolution of XPS core level spectra of Al 2*p* peak with MgF₂ and Al deposition. The binding energy is relative to the Fermi level. (b) Similar evolution of O 1*s* peak and (c) N 1*s* peak.

the main peak. This indicates that the chemical state of the Al atom in Alq₃ was altered by the deposition of MgF₂. As observed in the rest of the spectra in Fig. 2(a), the deposition of Al on MgF₂/Alq₃ creates initially only a single shoulder peak, although the strong peaks at 72.2 eV and 74.9 eV corresponding to the metallic Al and its oxide, respectively, eventually dominate at high Al coverages. The appearance of metallic Al 2*p* peak between 0.5 nm and 1.0 nm of Al coverage coincides with the observation of Fermi edge in the valence spectra in Fig. 1(b). The evolution of the O 1*s* peak shown in Fig. 2(b) also shows a similar trend. The bottom spectrum shows a single O 1*s* peak at about 531.6 eV from O atoms in pristine Alq₃. The deposition of MgF₂ creates an extra peak at higher BE side of the main peak. The separation between the main and the extra peak is about 1.2 eV. The deposition of Al on MgF₂/Alq₃ does not initially cause appreciable change, but at higher Al coverage, the broad peak originated probably from aluminum oxides dominates as the features from Alq₃ and MgF₂ deposition are buried

under the thick Al layer.

The evolution of N 1*s* peak is shown in Fig. 2(c). The deposition of MgF₂ on Alq₃ does not seem to cause any significant change in this peak except for the slight peak position shift. The deposition of Al on MgF₂/Alq₃ does not affect the position of the peak either. However, the formation of very weak extra peak in lower BE side of the peak was observed. At higher coverages of Al, the peak attenuates and broadens. Although not shown here, the C 1*s* peak did not show any changes throughout the deposition processes. The Mg 2*p* and the F 1*s* peaks from deposited MgF₂ did not indicate any meaningful change upon deposition of Al on MgF₂/Alq₃, except that the F 1*s* peak shifted slightly to a higher BE direction at Al coverage of 0.01 nm.

Although a similar OLED performance enhancement was observed in both Al/LiF/Alq₃ system and Al/MgF₂/Alq₃ system compared with Al/Alq₃ system, above observations suggest that the electronic structure of Al/MgF₂/Alq₃ interface is quite different from that of Al/LiF/Alq₃. First, movement of E_F relative to the vacuum level (or the valence band peak shift relative to E_F) in Al/MgF₂/Alq₃ occurs when MgF₂ is deposited and the MgF₂ deposition does not form gap states. Deposition of Al on MgF₂/Alq₃ does form gap states, but no peak shift is observed. This implies that the formation of gap states is not a necessary condition for the E_F shift. It appears that the E_F shift, not the formation of gap states, is responsible for the improved OLED performance by pulling down the lowest unoccupied molecular orbital (LUMO) level relative to E_F . Second, the formation of gap states in valence band does seem to accompany interaction between the deposited Al and N atoms in Alq₃. However, judging from the intensity of the extra peak, the interaction seems to be very weak. It is certainly not as strong as when Mg was directly deposited on Alq₃.^[5] Third, the deposited MgF₂ chemically reacts with Al and O atoms in Alq₃. Whether

MgF₂ is dissociated when it was deposited on Alq₃ is not clear at this stage. However, from the fact that both Al 2*p* and O 1*s* exhibit extra peaks at higher BE side, it can be said that both Al and O atoms lose electronic charges when MgF₂ interacts with Alq₃. Judging from the core level peaks, there is no indication that these charges were transferred to other atoms in Alq₃. Thus, it seems reasonable to think that they were transferred to either MgF₂ or its fragments, if they exist. Previous studies indicate that the deposition of Mg on Alq₃ creates an extra peak in N 1*s* core level peak just like other similar systems.[15] We observed only very weak such extra peak in N 1*s* when Al was deposited on MgF₂/Alq₃. Whether this is due to the dissociated MgF₂ or some other origin is not clear because Al deposition directly on Alq₃ also exhibited such weak extra peak in N 1*s* peak as well as weak gap states.[14]

In summary, we have studied the interface electronic structures of Al/MgF₂/Alq₃ using UPS and XPS. The valence band shift occurred when MgF₂ was deposited even before Al deposition and the concomitant gap state formation. The MgF₂ strongly interacted with Al and O atoms in Alq₃ before Al was deposited. The deposition of Al on MgF₂/Alq₃ formed gap states and only very weak extra peak in N 1*s* core level peak. These results indicate that the Al/MgF₂/Alq₃ interface is different from Al/LiF/Alq₃ and other LWFM/Alq₃ interfaces, although improvements in OLED performance were commonly observed.

This work was supported in part by the MOST of Korea through the NRL program and the Atomic-scale Surface SRC. DYK acknowledges the support by the Hallym Academy of Science, Hallym University.

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