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HREELS study on the interaction of MgF$_2$ with tris(8-hydroxy-quinoline) aluminum

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Abstract

The interaction between MgF$_2$ and tris(8-hydroxy-quinoline) aluminum (Alq$_3$) has been studied using high-resolution electron-energy-loss spectroscopy (HREELS). The reaction between MgF$_2$ and Alq$_3$ occurred in the cases of both MgF$_2$ deposited on Alq$_3$ and Alq$_3$ deposited on MgF$_2$. The shift of the loss peak corresponding to the out-of-plane ring bend was observed similar to that for Mg deposited on Alq$_3$. The HREELS spectra indicated that Mg was produced from MgF$_2$ deposited on Alq$_3$, and interacted with Al, O, and N in Alq$_3$. Analysis of the HREELS results suggested that Mg was not in the Alq$_3$ molecule plane.
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1. Introduction

Since the discoveries of efficient electroluminescence from organic molecules [1,2] intensive research concerning the physics and chemistry involved in organic light-emitting devices (OLEDs) has been carried out. 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. ITO glass, modified with an oxidative surface treatment, is commonly used as the hole-injecting contact [3–9], while a low work function metal or a metal alloy is used to form an effective electron-injecting contact [10–12]. The low work function metals are normally poorly suited for a production environment because of their extremely high chemical reactivity. The ability to transition to Al cathodes would represent a significant advance in the practical development of OLED devices. However, Al forms a rather poor cathode with most common electron transport materials resulting in high drive voltage and low efficiency for electron injection into tris(8-hydroxy-quinoline) aluminum (Alq$_3$). A

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significant step towards overcoming this problem was realized with the discovery that a very small amount of insulators, such as MgF_2, LiF, MgO, and Al oxides, introduced at the Alq_3/Al interface drastically improved both the drive voltage and luminescence efficiency [13]. Study on the interaction of the insulator layer with Alq_3 is important to understand the mechanism with which the insulating layer improves the OLED performance.

Previous studies using ultraviolet photoelectron spectroscopy (UPS) showed the gap state forma-

tion, and X-ray photoelectron spectroscopy (XPS) revealed the Al and O core level shift upon MgF_2 deposition onto Alq_3. These results indicate that the interaction mechanism in MgF_2/Alq_3 is different from that found in LiF/Alq_3 and other metal/ Alq_3 system. The reaction between MgF_2 and Alq_3 occurred when MgF_2 was deposited on Alq_3, with MgF_2 strongly interacting with the Al and O atoms in Alq_3 [14]. In this Letter, we present the application of high-resolution electron-energy-loss spectroscopy (HREELS) to study the vibrational
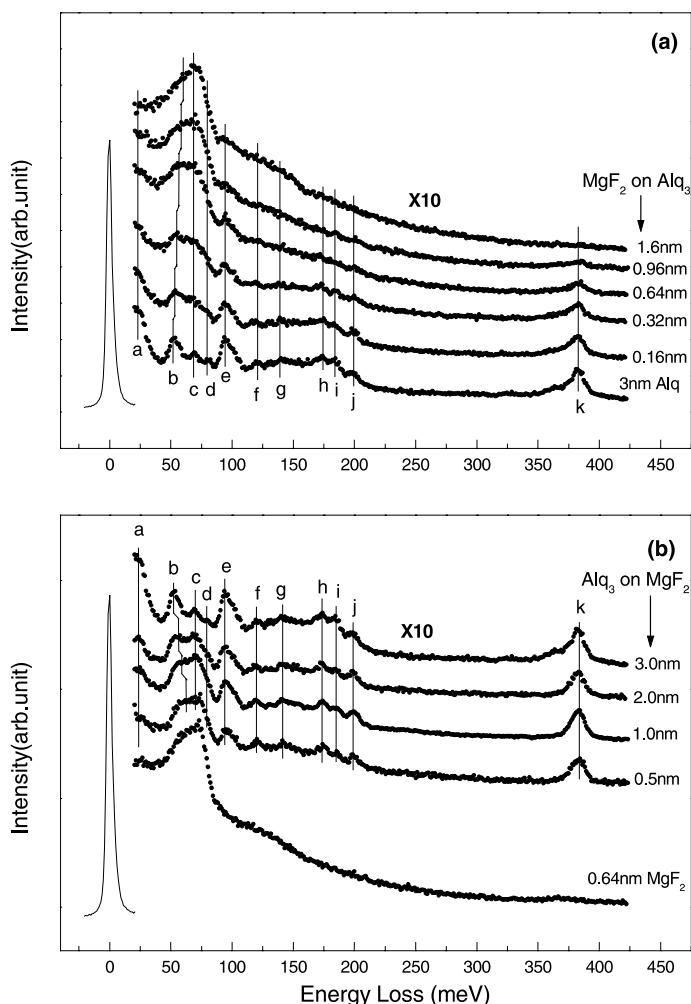

Fig. 1. (a) HREELS spectra collected for different amounts of MgF_2 deposited on the Alq_3 film. (b) HREELS spectra collected for different amounts of Alq_3 deposited on the MgF_2 film.

spectra of the Mg/Alq$_3$ system as well as the interaction of MgF$_2$ with the Al and O atoms in Alq$_3$.

2. Experimental

The HREELS measurements were performed in a LK Technologies Model ELS3000 HREELS spectrometer. The spectra were collected in a specular geometry with an incident and exit angle of 62° from the surface normal. The primary electron energy was 6.0 eV, and the resolution was set to be about 5 meV. Base pressure in the chamber was about 2×10^{-10} Torr.

A piece of Si crystal was chosen as the substrate making use of its smooth and stable surface. The Si was cleaned by annealing in the UHV chamber. The Alq$_3$, MgF$_2$, and Mg sources, purified by careful degassing, were deposited on the substrate under UHV condition in the evaporation chamber at a base pressure of better than 1×10^{-9} Torr, and the deposited sample was transported to the main analysis chamber without breaking vacuum. The thickness of the deposited film was determined by a quartz crystal microbalance.

3. Results and discussions

Fig. 1a shows HREELS spectra collected for different amounts of MgF$_2$ deposited on Alq$_3$ films. The spectrum at the bottom showed well-pronounced features of Alq$_3$. The assignments of the loss peaks for Alq$_3$ were reported previously [15]. The peaks, labeled a to k, were assigned to the different vibrational modes of Alq$_3$, which are related to ring pucker, out-of-plane ring bend, in-plane ring bend, out-of-plane C–H bend, ring breath, in-plane C–H bend, three ring stretch, and C–H stretch, respectively [15].

After MgF$_2$ was deposited on the Alq$_3$ layer, clear changes were observed in the HREELS spectra (the upper five spectra in Fig. 1a). First, the intensities of the loss peaks corresponding to the Alq$_3$ layer are reduced. Second, the loss peak b, which is related to the out-of-plane ring bend, shifts to the higher energy loss side. The shift of the loss peak b can also be observed when the experiment was repeated with an opposite deposition sequence (i.e., Alq$_3$ deposited on MgF$_2$, Fig. 1b), and the loss peak b shifted to the same peak position of pure Alq$_3$ (lower energy loss level). To
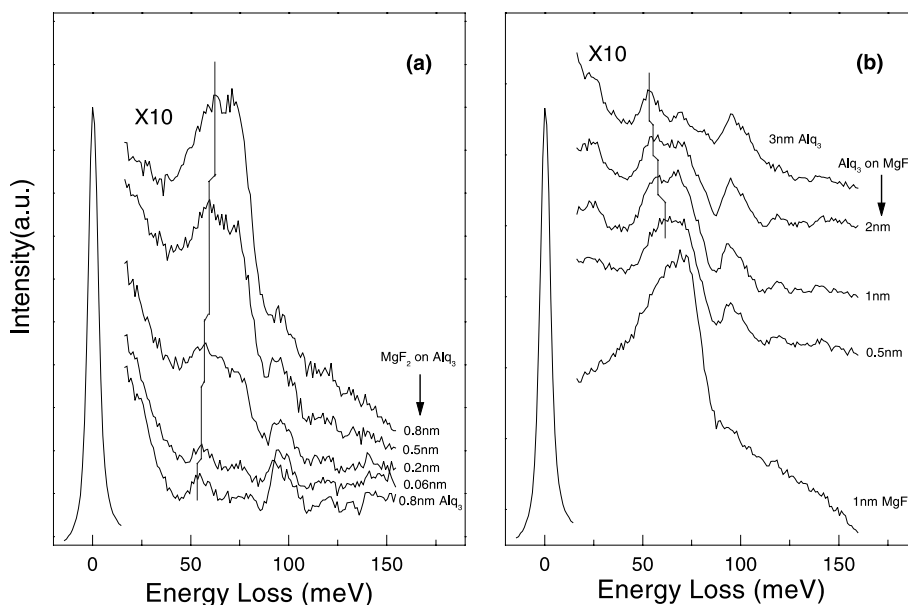

Fig. 2. (a) HREELS spectra collected for different amounts of MgF$_2$ deposited on the Alq$_3$ film. (b) HREELS spectra collected for different amounts of Alq$_3$ deposited on the MgF$_2$ film.

have a clearer view of this shift, those two experiments were repeated and the spectra were recorded in a narrow energy loss range (Figs. 2a,b). The spectra show that the loss peak b shifts about 7 meV to the higher energy loss side in Fig. 2a and shifts the same amount to the lower energy loss side in Fig. 2b.

Figs. 3a,b show the HREELS spectra taken after depositing Mg on the Alq_3 layer. The same shift of the loss peak b, related to the out-of-plane ring bend was observed, while the positions of other peaks remained unchanged. The HREELS results indicated that the interaction between Alq_3 and MgF_2 is similar to that between Alq_3 and Mg.
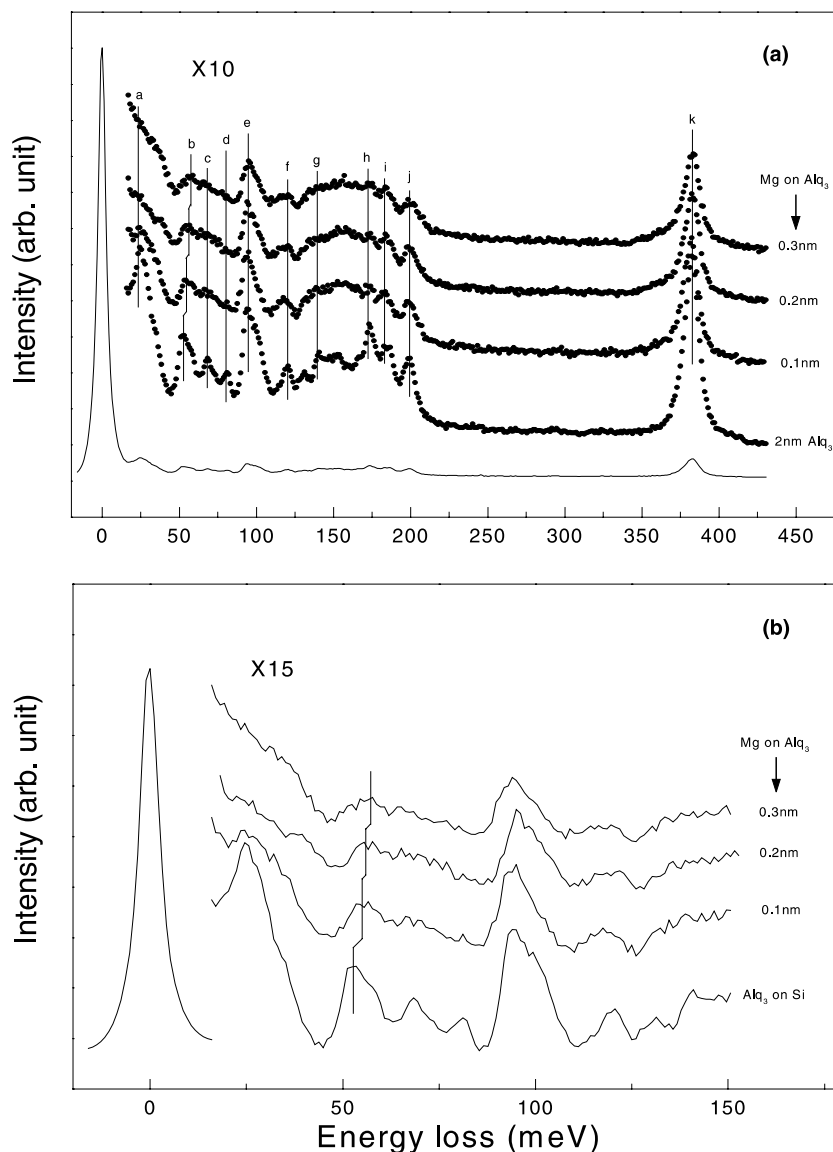
Fig. 3. HREELS spectra collected for different amounts of Mg deposited on the Alq_3 film.

This suggests that Mg was released upon MgF_2 deposition on Alq_3 and then interacts with Alq_3.

The structure of Alq_3 has been well determined [16–19] as shown in Fig. 4a. Its three-dimensional structural characteristics suggest that the Mg atom produced from the reaction can interact with any atom in the Alq_3 molecule. Eight representative structures of the Mg–Alq_3 interaction system, selected from the 18 possible cases [20], are shown in Figs. 4b–i. Structures b–e represent the cases where the Mg atom interacts with a benzene ring. For such cases, the addition of the Mg atom results in simple bonding, which causes only slight structural deviations from the original Alq_3 molecule. For structures f–i, the Mg atom inserts close to the core of the Alq_3 molecule or forms a bond with the Al atom, because the Mg atom is placed near the N or O atom or both and also the central Al atom. Therefore, the ensuing changes in structural configuration are substantive.

When the Mg atom bonds to the carbon atoms within an individual quinoline unit, the vibration energy of the out-of-plane ring bend should be reduced from the increasing mass consideration. Since the energy loss peak corresponding to the out-of-plane ring bend shifts to higher energy loss level, the structures produced from the Mg atom bonding to the carbon atoms within an individual quinoline unit as in the cases of b–e are less probable, even when a bond is also formed between the Mg atom and a N atom.

Previous XPS study of Park et al. [14] showed that the Al, O, and N core levels shift upon MgF_2 deposition on Alq_3. They reported that the Mg atom, produced from MgF_2, strongly interacted with the Al and O atoms, but weakly interacted with N in Alq_3. We have done similar XPS measurements on MgF_2 deposition on Alq_3, and our results are in complete agreement with those of Park et al. Therefore, both sets of XPS results
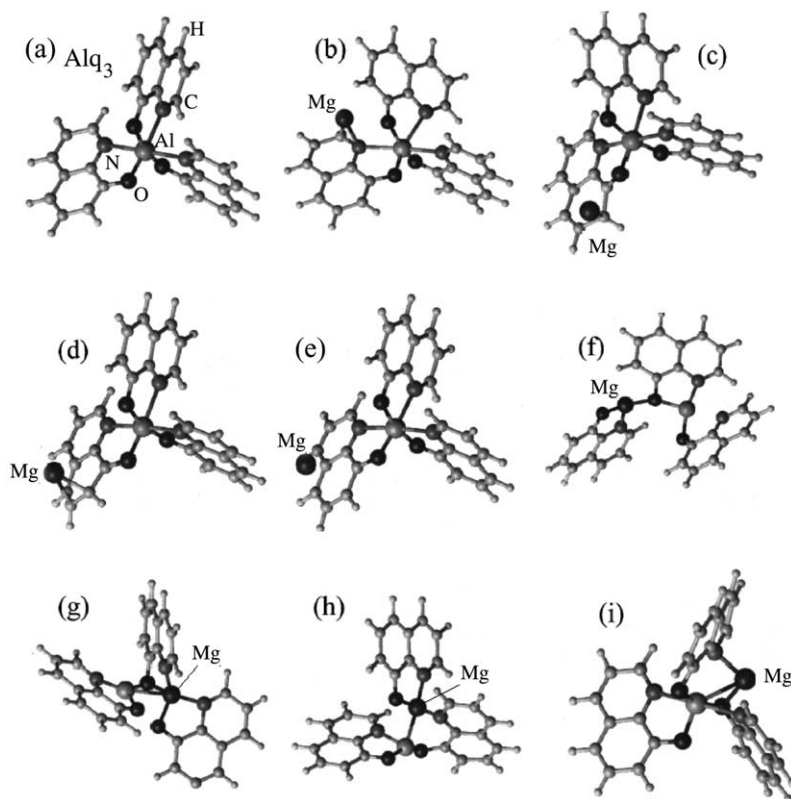

Fig. 4. The structural geometries of Alq_3 (a) and eight Mg–Alq_3 interaction systems (b)–(i).

support our analysis above that the cases b–e are less probable. While XPS results showed that the Mg atom bonds with the Al, O, and N atoms in Alq$_3$, they nevertheless could not tell how or in what configuration the Mg atom bonds to the Al, O, and N atoms. There are several possible configurations or interaction modes, as shown in Figs. 4f–i. With a strong Mg interaction with Al and O but a weak Mg interaction with N, the ring bend vibrations should be enhanced. Thus the energy loss peaks, corresponding to the ring bends, should shift to higher energy loss as revealed by the HREELS results. Since shifts occur only in the loss peak corresponding to the out-of-plane ring bend but not to the in-plane ring bends upon deposition of MgF$_2$ on Alq$_3$, the three interaction modes, shown in Figs. 4f–h, may be excluded. This is because if Mg interacts with Al, O, or N in the Alq$_3$ plane, such as that shown in Figs. 4f–h, the energy loss peaks corresponding to both the out-of-plane ring bends and in-plane ring bends will shift. The HREELS spectra show that only the peak corresponding to the out-of-plane ring bend shifts, while the peak corresponding to the in-plane ring bend does not. It suggests that the Mg atom interacts with Al, O, or N out of the interacted quinoline plane, such as shown in Fig. 4i.

After it is released from MgF$_2$, Mg interacts with Al, O, or N in the Alq$_3$ in the same manner as in the case of Mg deposited on the Alq$_3$ layer. The question then arises as to how F interacts with the Alq$_3$. The F may interact with C in an individual quinoline unit, similar to what hydrogen atom does. Since no changes of other loss peaks were observed, the frequency of F–C in an individual quinoline unit might be too low to be observed.

Acknowledgements

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