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Energy structures and chemical reactions at the Al/LiF/Alq$_3$ interfaces studied by synchrotron-radiation photoemission spectroscopy

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The chemical properties and energy levels of Al/LiF/Alq$_3$ were investigated via high-resolution synchrotron-radiation photoemission spectroscopy. No clear chemical reaction was found with LiF deposited on Alq$_3$. The core-level spectra show that Li$^+$ ion and Alq$_3$ anion are created only after Al is deposited on LiF/Alq$_3$ surfaces. Combined with the increase of the electron concentrations indicated by the Fermi-level position in valence-band spectra, the results provide direct evidence of the proposed chemical reaction, $3\ \mathrm{LiF}+\mathrm{Al}+3\ \mathrm{Alq}_3 \rightarrow \mathrm{AlF}_3+3\ \mathrm{Li}^+\mathrm{Alq}_3^-$, which leads to the excellent electron injection efficiency in Al/LiF/Alq$_3$. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2135376]

Conducting organic materials have attracted a lot of attention in recent years due to their applications in optical-electronic devices, such as organic light-emitting diodes (OLEDs) (Refs. 1–3). A typical OLED consists of multiple organic layers sandwiched by an anode and a cathode. Among the organic materials used in OLEDs, tris-(8-hydroxyquinoline)-aluminum (Alq$_3$) has been widely used and extensively studied because of its excellent luminescence properties and good stability. However, the performance of the OLEDs is not only determined by the luminescence efficiency of organic materials, but also strongly depends on how the carriers are injected from the metal electrodes into the organic materials. The energy alignment and chemistry at the interfaces between electrodes and organic thin films are the key elements that determine the charge transportations across the heterojunctions and hence would have a strong effect on the efficiency of OLEDs.

Although low work-function metals, such as magnesium or calcium, are theoretically preferred as cathode materials, aluminum has been broadly used due to better stability and manufacturability. The relatively high work function of aluminum cathodes, however, results in poor electron injection efficiency and higher operation voltage. Ultrathin layers of LiF, less than 1 nm, have been used as the inserting layers between Alq$_3$ and aluminum cathodes to improve the electron injection efficiency.[4,5] However, the mechanisms of the improved carrier injections with Al/LiF cathodes are still under debate. Some studies have suggested that the formation of effective cathodes is due to the release of Li ion from LiF in the Alq$_3$ matrix and the formation of Alq$_3^-$ anion through the thermodynamically favored reaction of $3\ \mathrm{LiF}+\mathrm{Al}+3\ \mathrm{Alq}_3 \rightarrow \mathrm{AlF}_3+3\ \mathrm{Li}^+\mathrm{Alq}_3^-$ (Refs. 6–8). This reaction leads to formation of n-doped Alq$_3$ at the interfaces and consequent enhancement of electron injections. Some recent studies, yet, conversely proposed different models. Lee *et al.* believed, via photoemission spectroscopy studies, that the highest occupied molecular orbital (HOMO) level lowering could be induced by the deposition of LiF on the Alq$_3$ layer *before* the Al deposition.[9] Song and his co-workers found partial substitution of hydroxyquinoline ligands of Alq$_3$ by F$^-$ ions and the formation of hydroxyquinoline anions at the Alq$_3$ interfaces upon LiF deposition, without subsequent Al deposition.[10] Ihm *et al.* also showed that the HOMO level lowering is due to the band bending caused by charge redistribution driven by the work-function difference between LiF and Alq$_3$, and *not* because of the chemical bonding of dissociated fluorine in the Alq$_3$ layer.[11]

The key issue causing these uncertainties is the lack of direct evidence of if and how Li$^+$ anions are formed at such interfaces. Most of the x-ray photoemission (XPS) experiments conducted in the previous works were carried out with high-energy photons at the order 1000 eV, such as Al $K\alpha$ (1486.6 eV) or Mg $K\alpha$ (1253.6 eV) photon lines, which have relatively small cross sections with Li 1s core level. As a result, very few clear Li 1s core-level information at the interfaces of Al/LiF/Alq$_3$ was reported, leading to the questions about the Li species at the interfaces. To make an unambiguous conclusion of the chemical reactions and the band structures at the Al/LiF/Alq$_3$ interfaces, Li 1s and Al 2p core-level spectra with high resolution and good signal-to-noise ratio are needed. In this letter we present the results from the synchrotron-radiation photoemission studies of Al/LiF/Alq$_3$ with probing photon energy at a soft x-ray region of 40–160 eV. The photon lines at this energy range have comparatively high cross sections for Li 1s and Al 2p core level, which enables us to obtain the information of the reaction of Li atoms at the interfaces. Our results reveal that very little chemical reaction and band movement occurs when LiF only is deposited on Alq$_3$. The Li$^+$ anion and n-doped Alq$_3$ are observed immediately after Al is deposited on LiF/Alq$_3$ surfaces.

All the photoemission experiments were performed at National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, R.O.C., and at National Taiwan University. The monochromatic photons were provided by a low-energy spherical grating monochromator (LSGM). The photon energy provided by the LSGM ranges from 20 to 160 eV. The

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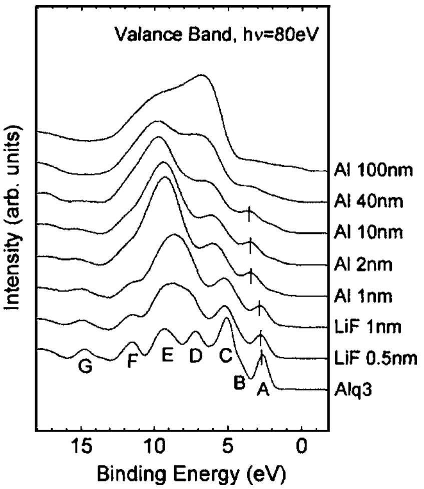

FIG. 1. The onset and valence band of photoemission spectra as a function of incremental deposition of LiF and Al.

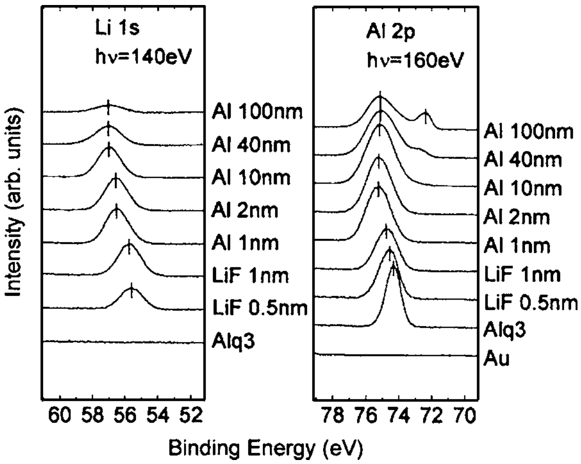

FIG. 2. The photoemission spectra of Li 1*s* and Al 2*p* core levels with LiF and Al deposition on Alq_3.

photoemission spectra of valence electrons were measured with a photon energy of 40 eV. The energy spectra of photoelectrons were collected with a 125-mm hemispherical analyzer with an overall resolution better than 0.05 eV. Aluminum and lithium fluoride were evaporated from the OMICRON EFM3 electron-beam evaporators. Organic thin films were thermally evaporated and deposited *in situ* on gold-coated silicon substrates. All the depositions were carried out in the ultrahigh-vacuum photoemission chamber with a base pressure of 5×10^{-11} Torr. The Fermi level of the system was measured on the gold surface before the organic thin-film deposition. The core-level spectra of lithium fluoride and aluminum atoms, i.e., Al 2*p*, Li 1*s*, and F 2*s*, were excited with 80 eV to 140 photons to ensure a high count rate and good surface sensitivity.

Figure 1 shows the valence-band spectra as a function of incremental deposition of LiF and Al. The energy position of HOMO, the rising edge of peak *A*, of pristine Alq_3 on gold surface is 1.8 eV below the Fermi level. With an Alq_3 band gap of 2.8 eV, the Fermi level is a little bit above the midgap of pure materials. The vacuum level, obtained from the onset of the photoemission spectra, is about 4.6 eV above Fermi level. The ionization energy (IE), which is the energy difference between the HOMO and vacuum levels, of Alq_3 is about 5.6 eV, similar to the reported data.[12–14] The origins of the features *A*–*G* in the valence spectra were explained in our previous report.[15] With LiF deposited on Alq_3, the HOMO position slightly shifts toward higher binding energy by less than 0.1 eV. The energy positions of most of the occupied levels, including peaks *A*, *C*, *F*, and *G*, also do not change significantly. Peaks *D* and *E* at 8–10 eV are overlapped by a large and broad peak related to the stronger density of states of F 2*p* valence band.[16] There is no significant evidence indicating that the electronic structures of Alq_3 are being altered until the deposition of Al. With only a little Al, it is very clear that the HOMO peak, as well as other peaks, shift toward higher binding by about 1 eV. This shift indicates that the Fermi level moves up from 1.8 to 2.8 eV above HOMO, close to the edge of the lowest unoccupied molecular orbital (LUMO) level, implying that the electron concentration increases in the Alq_3 matrix and the material is heavily *n* doped after Al deposition. The closer alignment of the metal Fermi level and LUMO of Alq_3 makes the electron injection more efficient and hence improves the device performance. An extra gap state is also found at the interfaces of Alq_3 and LiF with the existence of Al. It is noteworthy that even at 40 nm of Al coverage the valence-band spectra still exhibit features of Alq_3, indicating Al clustering on the surfaces. Still, the underlying mechanisms creating the *n*-doped status of Alq_3 need to be found out with core-level photoemission spectra.

The photoemission spectra of the Li 1*s* and Al 2*p* core level with LiF and Al deposited on Alq_3 were shown in Fig. 2. Spectra were taken *in situ* immediately after each deposition. The incremental depositions of LiF and Al were carried out so that the interface reaction can be investigated via photoemission spectroscopy. As shown at the bottom spectrum in Fig. 2, the binding energy of the Al 2*p* core level of pristine Alq_3 is 74.4 eV. This energy is similar to the Al 2*p* binding energy in Al_2O_3 (Refs. 17 and 18) and AlN (Ref. 19), as aluminum atoms interacting with nitrogen and oxygen atoms in Alq_3 molecules. The deposition of LiF on Alq_3 only causes a slight shift of the Al 2*p* core level toward higher binding energy, indicating a slight change of chemical environment due to the arrival of foreign species. Upon the deposition of LiF, the Li 1*s* core level appears at the binding energy of 55.6 eV, which is consistent with the reported LiF binding energy.[20] Combined with the minimal change (less than 0.3 eV) of the Al 2*p* core level, the result indicates that there is no strong chemical reaction between LiF and Alq_3. We also will verify the binding energy of the Li 1*s* core level of nonreacted LiF in the latter part of this letter. The deposition of Al, however, changes both Li 1*s* and Al 2*p* core-level spectra drastically. The Al 2*p* core levels shift from 74.7 to 75.3 eV, indicating the formation of AlF_3 right after the Al deposition at room temperature. The Li 1*s* core level moves about 1.4 eV toward higher binding energy, at 57.1 eV. The extremely high binding energy of the Li 1*s* core level implies the heavily and positively charged Li species, i.e., Li^+ ion. The excess electrons are therefore transferred to the Alq_3 matrix with Li^+ ions blended in. Along with the increase of the electron concentrations found in valence-band spectra, the results above are the direct evidence of the following chemical reaction of $3\,LiF+Al+3\,Alq_3\rightarrow AlF_3+3\,Li^+Alq_3^-$ (Refs. 6–8). With continuing Al deposition, the metallic Al 2*p* core level finally appears at 72.3 eV. The separation of the Al 2*p* core level of metallic Al

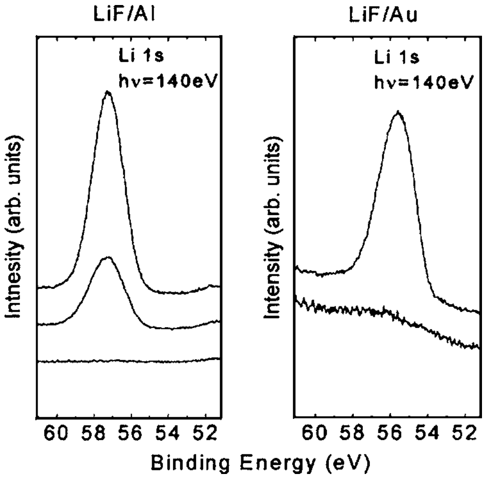

FIG. 3. Li 1*s* core-level spectra of 0, 0.5, and 1 nm of LiF deposited on Al (left) and 0 and 1 nm of Lif on Au (right). The binding energy of the Li 1*s* core level is 57.2 and 55.6 eV with LiF deposited on Al and Au, respectively.

and AlF_3 is consistent with the reported value of about 3 eV.

There might be questions regarding whether the Li 2*p* core-level shift after Al deposition is due to band bending or a chemical shift. Furthermore, there also have been doubts about whether LiF decomposed during the evaporations. To further clarify these points, the photoemission spectra were taken on the samples with LiF deposited onto Al and Au substrates, as shown in Fig. 3. With LiF deposited on Au, where no reaction is expected, the Li 1*s* core level is found at the binding energy of 55.6 eV, which is consistent with the reported LiF data. It shows that LiF is evaporated without decomposition. As for LiF deposited on Al substrates, the Li 1*s* core level is found at 57.2 eV, similar to that in the $Al/LiF/Alq_3$ samples. The results confirm that the extreme high binding energy of Li 1*s* shown in the previous section is truly due to the chemical reaction, and that the energy shift in the photoemission spectrum is not because of bend bending.

In summary, we carried out a detailed study of chemistry and energy structures at the interfaces of the $Al/LiF/Alq_3$ trilayer with high-resolution synchrotron-radiation photoemission spectroscopy. The formation of AlF_3, Li^+ ion, and *n*-doped Alq_3 were found upon the deposition of Al on LiF/Alq_3 thin films. The investigation provides direct evidence of the chemical reaction $3\ LiF+Al+3\ Alq_3 \rightarrow AlF_3 + 3\ Li^+Alq_3^-$, which leads to the excellent carrier injection of the $Al/LiF/Alq_3$ trilayer.

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