

Electronic structure and energy level alignment of Alq₃/Al₂O₃/Al and Alq₃/Al interfaces studied by ultraviolet photoemission spectroscopy

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Abstract

The electronic structures at the interface of aluminum tris(8-hydroxyquinoline) (Alq₃)/Al₂O₃/Al have been determined by ultraviolet photoemission spectroscopy measurements and compared to similar measurements of the Alq₃/Al interface. In the Alq₃/Al₂O₃/Al study, shift of the highest occupied molecular orbital level of the Alq₃ layer was observed when compared to that of Alq₃/Al. An energy level alignment diagram was proposed, showing that the lowering of the driving voltage achieved in organic electro-luminescent devices with a thin Al₂O₃ layer between the aluminum cathode and the Alq₃ film can be attributed to the reduction of the barrier height for electron injection. The electronic structures of Alq₃ grown on Ga and its oxide have also been studied. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Energy level alignment; Organic light emitting devices; Barrier height; Buffer layer; Photoemission

1. Introduction

Recently applications of various organic semiconductors, such as small molecules and various π -conjugated polymers which are two important classes of electroluminescent materials, to light emitting devices have drawn wide attention due to their potential use in multicolor flat panel displays [1,2]. Besides proper selection of organic materials, it is generally agreed that efficient carrier injection from both electrodes plays a key role in achieving the best device performance. In order to understand the mechanism of the carrier injection, band-structure diagram has always been used to explain behaviors of the injected electrons and holes for organic light emitting devices (OLEDs) [3,4]. Thus, the importance of properties of the interfaces between the organic layer and the electrode has been established. Extensive published studies have suggested that one of the dominant mechanisms for carrier transport across the interface is tunneling [5,6]. The potential barrier heights at interfaces of OLEDs are, therefore, the important parameters which govern the efficiency of the carrier injections. In this regard, any metal that has a low work-function, such as Ca ($\phi = 2.8$ eV) and Mg ($\phi = 3.66$ eV), is a good choice for obtaining a small potential barrier height at interface between organic material and cathode material. However,

such devices turn out to be unstable. This is mainly due to the reactive nature of these metals in air.

Although a cathode consisting of aluminum with a higher work function ϕ of 4.3 eV is stable, the OLEDs that have Al cathodes are much less efficient than the devices that use low work-function metal cathodes [7]. As an alternative, insertion of an ultrathin insulating layer of LiF between the Alq₃ layer and the Al cathode leads to significant enhancements of the current injection and electroluminescence (EL) output [7,8]. Besides LiF, other materials such as CsF, Al₂O₃, MgO and GeO₂ have been introduced between organic layer and Al cathode [8–10]. However, not all of the materials have led to significant enhancement in the current injection.

Recently, Li et al. reported that by inserting a suitably thick buffer layer of Al₂O₃ between Alq₃ layer and Al electrode, both the current injection and the electroluminescence output can be significantly increased [10]. Although they believed also that the barrier height play an important role for the reduction of the driving voltage, the barrier height at the Alq₃/Al₂O₃/Al interface could not be deduced from their experimental results. In this work, we use ultraviolet photoemission spectroscopy (UPS) to study samples consisting of sandwiched layers of Alq₃/Al₂O₃/Al. We shall discuss the change in the barrier height for electron injection when compared to similar two-layer samples consisting of just Alq₃ and Al. As our results show below, the lowering of the driving voltage in the organic LEDs can be ascribed to the reduction of the barrier height in the presence of the thin

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Al₂O₃ layer at the Alq₃/Al interface. We have also carried out similar measurements using Ga instead of Al but we were not able to obtain similar results, which shows that the effect of an insulating oxide layer between the Alq₃ and the metal layer cathode depends on the metal that is chosen.

2. Experimental details

The layer structure of Alq₃/Al₂O₃/Al was fabricated by vacuum evaporation of the organic films on the top of metal oxide. Due to the much lower temperature of the deposition and the higher stability of the metal and metal-oxide surfaces, these interfaces are more abrupt than those obtained by reverse deposition and lead to an easier acquiring of their electronic structures. Similar to the normal method of OLED preparation [10,11], an Al layer (~100 nm) was evaporated on an ultrasonically cleaned Si substrate in a vacuum chamber with a base pressure of 10⁻⁵ Torr. The Al₂O₃ layer was obtained by simple exposure of the Al film to the air for a duration of 5 min, similar to what Li et al. used in the practical fabrication process. Then the sample was transferred into an ultrahigh vacuum system (10⁻¹⁰ Torr) which was composed of an analysis chamber and a preparation chamber used for organic deposition. Prior to analysis by X-ray photoemission spectroscopy (XPS) to determine the thickness of the Al₂O₃ film, the sample was Ar⁺ bombarded for 75 s to eliminate possible contamination of the surface. Then, after the XPS measurements, a thin layer of Alq₃ was deposited on the sample by vacuum evaporation in the preparation chamber. Finally, the Alq₃-covered sample was transferred to the analysis chamber again for UPS measurements. Spectra were recorded using Al K_α excitation (1486.6 eV) for XPS and He I excitation (21.2 eV) for UPS study. The energy of the photoelectrons was analyzed by a concentric hemispherical-type electron energy analyzer, with an overall resolution of about 1 eV for XPS and 0.2 eV for UPS. Likewise, the latter structure of Alq₃/Al was formed in a similar manner except that, prior to evaporation of Alq₃, Ar⁺ bombardment cleaning was performed to eliminate the Al₂O₃ film which was detected by XPS measurement.

3. Results and discussion

In Fig. 1, XPS Al2p core level peaks of the Al film surfaces are shown. The upper figure shows the spectra of the Al film surface exposed to air for 5 min, while the lower figure shows the spectra of the Al film surface sputtered by Ar⁺ gun for about 20 min. The peaks at 1411.3 and 1413.8 eV are characteristic of Al oxide and metallic Al, respectively, which is consistent with the result obtained by Li et al. [10] We can clearly see the oxidation of the Al film after 5 min exposure. If we assume that the oxide layer covers the pure Al surface uniformly, the relationship between the

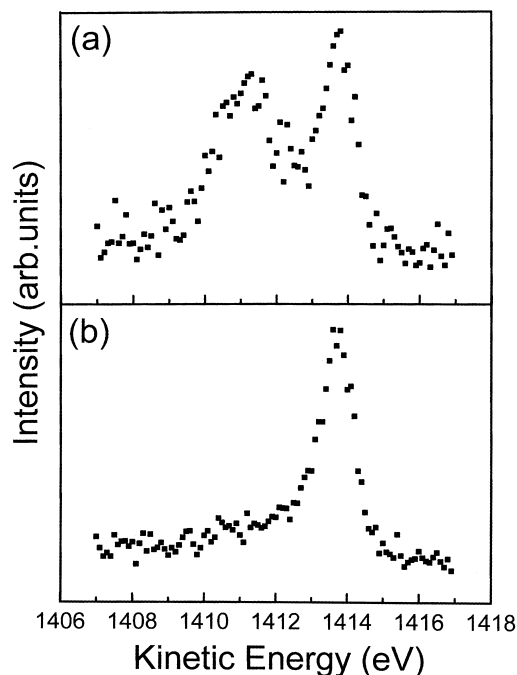


Fig. 1. (a) X-ray photoelectron spectra of Al surface exposed to air for 5 min (b) X-ray photoelectron spectra of cleaned Al surface.

integrated intensity of the oxide state of surface layer, I_s , and that of the bulk Al state, I_b , can be expressed as

$$I_s/I_b = [1 - \exp(-d/\lambda \cos \theta)] / \exp(-d/\lambda \cos \theta) \quad (1)$$

where d is the thickness of the Al₂O₃ layer, λ and θ are the mean-free path (~18 Å) and takeoff angle (~32°) of the photoelectrons, respectively. The calculated result indicates that a ~13 Å Al₂O₃ layer was formed on the top of the Al film, which is almost the required thickness to give significant reductions of the driving voltage of the organic LEDs [10].

Fig. 2 shows the UPS spectra of each layer. The thickness of the Alq₃ layer is no more than 1 nm, which was monitored by a quartz thickness monitor, thick enough to obtain the electronic states of the interface. The abscissa is the binding energy relative to the Fermi level of the Al layer. Though the Alq₃ layer is very thin, the obtained spectrum shows a reasonable agreement with the reported Alq₃ spectrum in shape [12,13]. The distinguishable peak closest to the Fermi level is ascribed to the highest occupied molecular orbital (HOMO) of Alq₃. The difference between the Fermi level of the metal and the highest occupied state (HOS) of Alq₃ was obtained from the UPS spectra which exhibits both characteristics of metal valence band structures and HOMO of Alq₃. The Fermi level was determined as the middle of the valence band edge of the metal while the HOS of Alq₃ was given by the intercept of the tangent line for the HOMO peak with the base line of the Alq₃ spectra [13]. It is worth noting that for the sample containing the oxide layer, the energy difference between the Fermi level and the HOS of Alq₃ layer was 2.4 eV. This is larger than that

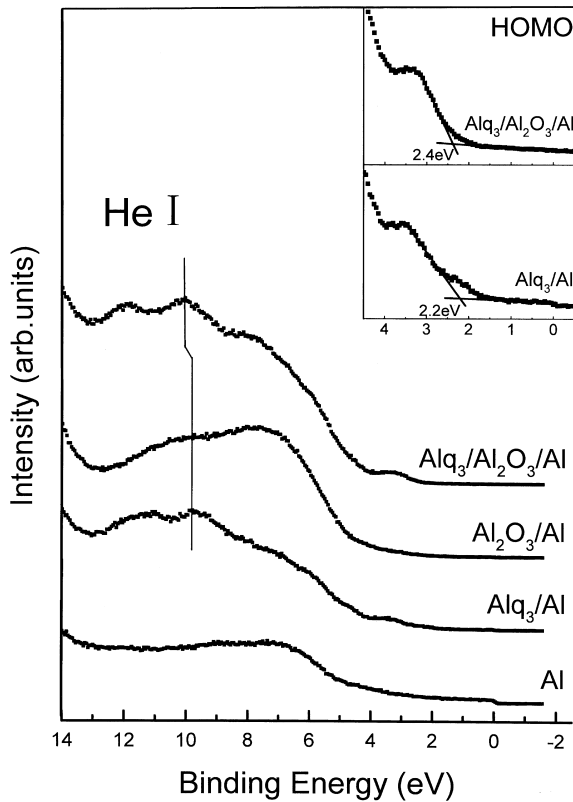


Fig. 2. UPS spectra of Al layer and of Alq₃ layer on Al, Al₂O₃ and Al₂O₃/Al layer.

of the sample without the oxide layer, where the difference is only 2.2 eV. The HOS of the Alq₃ layer was shifted to a higher binding energy due to the presence of the thin Al₂O₃ layer. Accordingly, the peaks of molecular levels with higher binding energies were 0.2 eV shifted, as shown in Fig. 2.

The vacuum levels of the samples were determined by linear extrapolation of the onset of secondary electrons on the low kinetic side of the UPS spectra, which were measured with the sample biased at -6 V to avoid the influence of the detector work function. The vacuum levels of Al, Alq₃ on Al, Al₂O₃ on Al and Alq₃ on Al₂O₃/Al were found to be 4.1, 3.3, 3.4 and 3.3 eV, respectively.

From these experimental results, the interfacial energy diagrams can be depicted as shown in Fig. 3. The ionization energy (IE) of Alq₃, which is defined as the energy of the HOS relative to the vacuum level, is 5.5 eV for Alq₃ on Al and 5.7 eV for Alq₃ on Al₂O₃/Al. The value is consistent with that reported in recent work [13–16]. From Fig. 2, a broadened HOMO peak and the emergence of new states above the HOMO can be observed in the spectra of Alq₃ on Al when compared to that of Alq₃ on Al₂O₃ which is highly chemically stable. Similar behavior is observed at interfaces of Alq₃/Mg and Alq₃/Ca [13,17]. This is deduced by the interaction between Alq₃ and the metal and is related to the shift of IE to a lower energy [18]. The energy of the lowest unoccupied molecular orbital (LUMO) edge of the

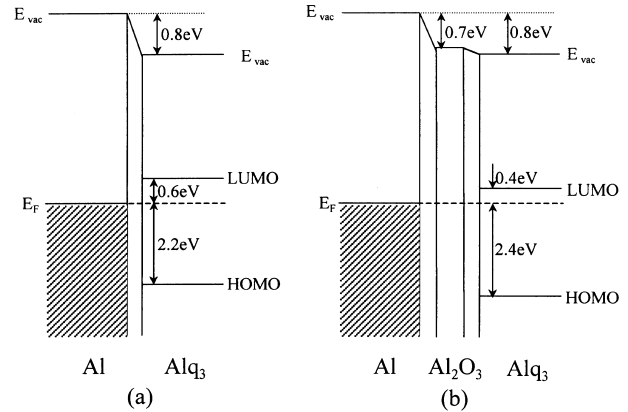


Fig. 3. Energy level alignment for (a) the Alq₃/Al interface and (b) the Alq₃/Al₂O₃/Al interface.

Alq₃ layer relative to the vacuum level can be obtained from the energy of the HOS and the observed optical band gap of Alq₃ which is 2.8 eV. If the influence of the dipolar potential at the interface on the electron injection is not considered, the energy difference between the Fermi level of the Al layer and the LUMO edge of the Alq₃ layer, which is defined as the barrier height for electron injection, is 0.4 eV for the Alq₃/Al₂O₃/Al interface and 0.6 eV for the Alq₃/Al interface. Therefore, the barrier height is reduced by about 0.2 eV by the buffer layers between the Alq₃ film and the Al cathode. This is one of important factors that significantly contributes to the lowering of the driving voltage in organic LEDs with such a cathode structure. This difference is not as large as the reduction (0.4 eV) introduced by inserting a thin

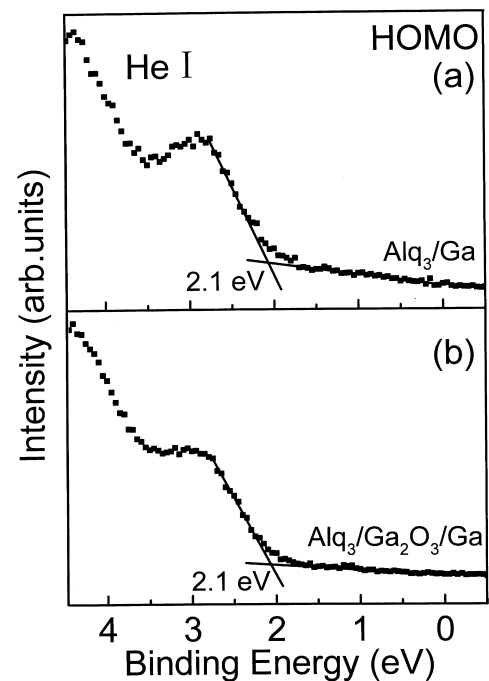


Fig. 4. (a) UPS spectra of the HOMO of Alq₃ layer on Ga (b) UPS spectra of the HOMO of Alq₃ layer on Ga₂O₃/Ga.

LiF layer instead of Al_2O_3 layer [14]. Therefore, one can conclude from above discussion that LiF is a better inter-layer for the improvement of electron injection from an aluminum cathode into the luminescent layer.

We have also studied the Alq_3/Ga and $\text{Alq}_3/\text{Ga}_2\text{O}_3$ interfaces in a similar manner. There is no distinct difference between the spectra of Alq_3 on Ga and Alq_3 on $\text{Ga}_2\text{O}_3/\text{Ga}$. The spectra of the HOMO of Alq_3 are exhibited in Fig. 4. There is less distinctness of the HOMO peak of the Alq_3 layer on $\text{Ga}_2\text{O}_3/\text{Ga}$ as compared to that of the Alq_3 on Ga. No shift of the HOMO level of the Alq_3 layer due to the insertion of a thin Ga_2O_3 layer was observed. The offsets between HOMO and the Fermi energy level are 2.1 eV for both spectra. This can be interpreted by the fact that Ga exhibits weak reactivity and interaction with Alq_3 which result in a slow diffusion into the Alq_3 layer at room temperature [19].

4. Conclusions

In summary, we have measured the electronic structures of $\text{Alq}_3/\text{Al}_2\text{O}_3/\text{Al}$, Alq_3/Al , $\text{Alq}_3/\text{Ga}_2\text{O}_3/\text{Ga}$ and Alq_3/Ga interfaces by ultraviolet photoemission spectroscopy. A shift of the HOMO edge of Alq_3 layer towards higher binding energy deduced by the thin Al_2O_3 buffer layer was observed, while no evident change of HOMO edge by a thin Ga_2O_3 buffer layer was detected. These results suggest that the insertion of an insulating oxide layer of a suitable material between the cathode and the Alq_3 layer can reduce the barrier height for electron injection, which significantly enhances the current injection in organic LEDs.

Acknowledgements

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