

Energy level alignment at Alq/metal interfaces

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The energy level alignment for both Mg/8-hydroxyquinoline aluminum (Alq) and Au/Alq interfaces has been determined by the ultraviolet photoemission measurements. For both interfaces, the difference between the Fermi level and the low-energy edge of the highest occupied molecular orbital (HOMO) is around 1.7 eV. This implies that the Fermi level with respect to the HOMO edge of Alq is independent of the work function of Mg and Au despite a large difference in the metal work function. A Fermi level alignment model is proposed, invoking a charge transfer between the metal and Alq and the formation of a dipolar layer at the metal/Alq interface. © 1998 American Institute of Physics. [S0003-6951(98)01213-3]

There is continuing interest in developing low-cost electronic devices¹⁻⁶ based on organic materials for various applications. Among these devices, organic light emitting diode (LED) or an electroluminescent (EL) device is perhaps the most promising because of its superior performance and potential application in flat-panel displays. An important device characteristic is the low drive voltage (<5 V), which is a direct consequence of the low-impedance contacts engineered for the LED. The LED structure generally consists of an indium-tin-oxide (ITO) as the anode and an evaporated metal film such as an Mg:Ag alloy as the cathode, sandwiching in between a thin layer or multilayer of organic films. The choice of these contacting electrodes is primarily governed by the work-function relationship, i.e., a high work-function metal (e.g., Au, 5.5 eV) for the anode and a low work-function metal (e.g., Mg, 3.7 eV) for the cathode, using the assumption of vacuum level alignment across the contact. This study is aimed at understanding the interfacial electronic structure of the metallic contact with 8-hydroxyquinoline aluminum (Alq), using photoemission (UPS) and x-ray photoemission (XPS) to examine the interface formation and the resulting energetics. Alq is chosen for the present study because it is the prototypical and most commonly used organic material in LED and represents the state-of-the-art electron transport/emitting layer. The principal result is that the measured energy offset between the Fermi level of the metal and the highest occupied molecular orbital (HOMO) of Alq is independent of the metal work function. We propose a model of dipole layer formation at the organic/metal interface to account for the energetic of the contact and its injection behaviors in the LED. Similar observations of possible dipole layer structure have been made on the electronic structure of porphyrin (ZnTTP)/metals⁷ and in dye/silver halide interfaces.^{8,9}

The UPS measurements were performed with samples biased at negative 4 V in an ultrahigh vacuum chamber with a base pressure $\sim 1 \times 10^{-10}$ Torr. The chamber was

equipped with an Auger electron spectrometer, a UPS spectrometer, and a rear-view low energy electron diffraction optics. The substrates used in the present experiments were ITO-coated glass. The substrates were first ultrasonically cleaned in a mixture of isopropyl alcohol and water (1:1) and then degreased in toluene vapor.¹ It was then transferred immediately from atmosphere to a deposition chamber (in about 10 min), which was attached to the analysis chamber and separately pumped by a molecular turbo-pump. The base pressure of the deposition chamber was about 5×10^{-9} Torr. Mg and Au were deposited from resistively heated tungsten boats and Alq from a tantalum boat. The thicknesses of the deposited layers were monitored by a quartz crystal micro-balance.

The difference between the Fermi level of the metal and the highest occupied state (HOS) of Alq was measured from the UPS spectrum which exhibits both the characteristics of the metal valence band structures and the HOMO for Alq. The Fermi level was determined at the middle of the valence band edge of the metal, while the HOS of Alq was given by the intercept of the tangent line for the HOMO peak with the baseline of the Alq spectrum after the contribution of the metal valence band was excluded.

Figure 1 shows the He I UPS spectra of Mg on Alq with different Mg overlayer thicknesses. The thickness of the Alq layer is 15 nm which was grown on ITO. The bottom spectrum exhibits the characteristic features of emission from the Alq film without the Mg overlayer. The distinguishable peak closest to the Fermi level is the Alq HOMO, which is 6.34 eV below the vacuum level. This value is about 0.3 eV smaller than that reported in a recent work.¹⁰ The ionization energy of Alq, which is defined as the HOS relative to the vacuum level, is 5.70 eV, which is comparable to the value of 5.66 eV obtained by Hamada *et al.*¹¹ With increasing Mg layer thickness, the sharp peaks of Alq become broadened. In addition, there is an energy shift in the Alq HOMO. Taking into account of the mixing of Mg and Alq UPS spectra and the possible influence of the background from secondary electrons, the position of the HOMO center is estimated to have shifted about 0.3 eV towards the higher binding energy

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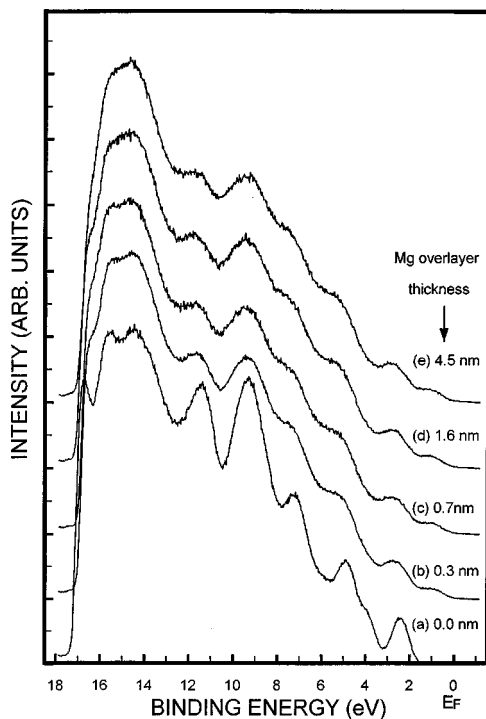


FIG. 1. The He I UPS spectra as a function of the thickness of Mg overlayer on Alq.

after Mg deposition. Such a shift in energy would normally be attributed to a surface band bending in the Alq. However, it has been determined that this shift is due to the charging effect in the UPS spectra due to the insulating nature of the Alq film.¹² The energy difference (band offset) between the Fermi level of metal and the HOS of Alq is 1.7 eV.

UPS spectra of the Au on Alq interface are shown in Fig. 2. The Fermi level was determined at the middle of the leading edge of the UPS spectrum for a 0.15 nm Au overlayer. At this Au thickness, the Alq spectral features are still clearly evident. The band offset between the Fermi level of Au and

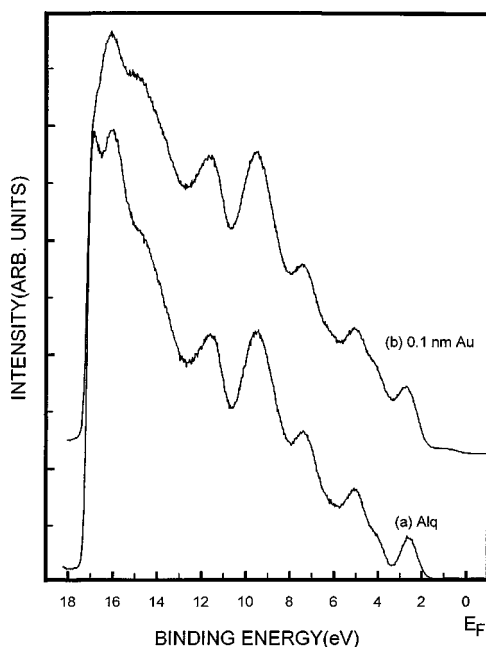


FIG. 2. The He I UPS spectra of (a) Alq and (b) of thin Au layer on Alq.

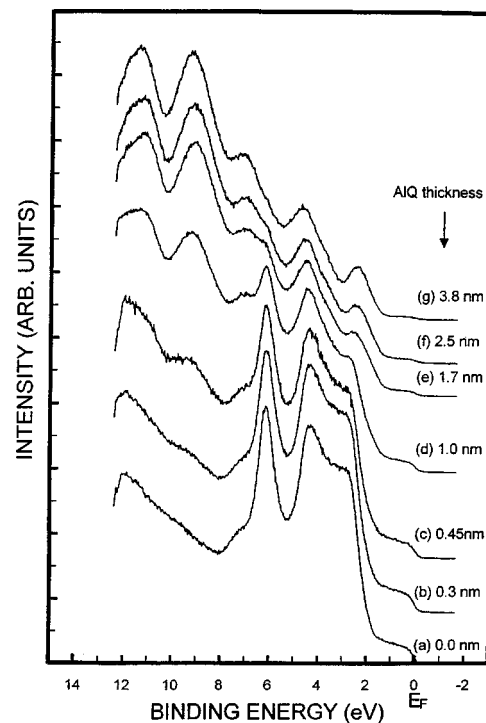


FIG. 3. The He I UPS spectra as a function of Alq thickness deposited onto thick Au film.

the HOS of Alq was readily determined to be 1.7 eV, which is the same as the value obtained from the Mg on Alq interface.

Figure 3 shows the UPS spectra of overlayers of Alq on Au. At thicknesses greater than 0.3 nm, features related to Alq below a binding energy of 9 eV emerge, while lower binding energy peaks for Alq are only apparent beyond 1.7 nm due to interference from the intense Au *d* band. The topmost spectrum in Fig. 3 shows the features from a thick (3.8 nm) Alq overlayer, which are superimposed on the much attenuated Au spectrum. The intensity of emission from the Fermi edge decreases with increasing thickness of the Alq overlayer, while the Fermi level positions remain unchanged. The band offset measured for the Alq on Au interface is also about 1.7 eV, which is the same as that obtained at the Au on Alq interface.

An energy level diagram for Alq/Au and Alq/Mg contact is depicted in Fig. 4. The work functions of Mg (Ref. 13) and Au (Ref. 14) are 3.66 and 5.1 eV, respectively, and the ionization potential I.P. for Alq is 5.7 eV. The band offsets for both contacts are 1.7 eV, as determined from the UPS data. Given these energetic values, a voltage drop and therefore a space charge layer must exist across the Alq/metal interface to compensate for the difference in vacuum energy levels between Alq and the contacting metal. This voltage drop ΔE as shown is -0.33 and 1.15 eV for Mg and Au, respectively. The width of this space charge layer, δ_i , and the corresponding surface charge density on the metal, Q_m , are related through the following equation¹⁵

$$\Delta E = -(e/\epsilon_i\epsilon_0)Q_m\delta_i,$$

where e is the electronic charge, ϵ_i is the dielectric constant of the interfacial layer, and ϵ_0 is the vacuum permittivity.

The sign of ΔE indicates a positive surface charge on Mg

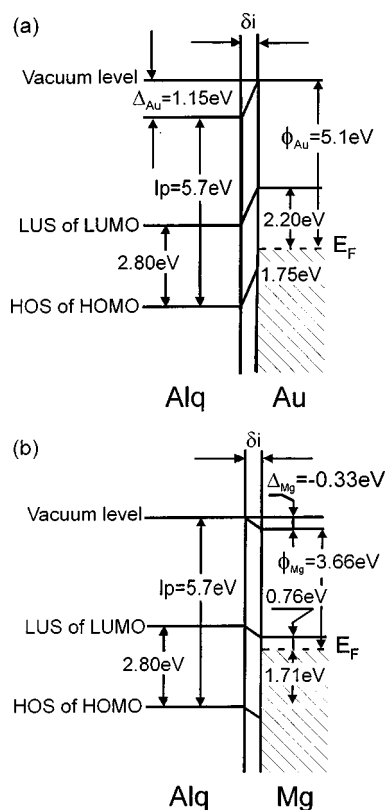


FIG. 4. The energy level alignment for (a) Al/Alq and (b) Mg/Alq interfaces.

and therefore a negative space charge on Alq. The reverse is true for the Alq/Au contact. This interfacial structure is presumably set up by the charge transfer from the metal to organic layer. In the case of Mg/Alq contact, the electron is donated from Mg to the Alq layer to form an equivalent of a dipolar $\text{Mg}^+ \dots \text{Alq}^-$ complex, the exact nature of which is not yet known. More recent experiments¹⁶ have indicated that the deposition of a reactive metal on Alq can result in chemical reaction between the metal and Alq with the first few angstroms of Alq. Thus, it is quite probable that the space charge layer is caused by such a reaction and therefore the width of the space charge layer is also of the order of a few angstroms, i.e., a monolayer of Alq. The abrupt nature of the space charge layer may also be a result of a large electron trap density in Alq,¹⁷ of the order of the molecular density. In either case, the charge transfer between Mg and Alq is limited to the interface, which means that the Fermi level is effectively “pinned” and the existence of a dipolar double layer with a width of a few angstroms is implied. The HOMO edge, or HOS of Alq in the bulk therefore remains constant at an energy of 1.7 eV with respect to the Fermi level. Taking the values of ϵ_i and δ_i to be 4 and 0.4 nm, respectively, the surface charge densities Q_m can be calculated to be $1.8 \times 10^{12}/\text{cm}^2$ and $-6.4 \times 10^{13}/\text{cm}^2$ for Mg and Au, respectively, from the measured values of ΔE 's. A similar model of charge transfer at metal/ C_{60} was proposed by Ohno *et al.*¹⁸ They reported that the band offset between the metal Fermi-level and the C_{60} HOMO edge was independent of the metal work function, implying an alignment of the Fermi level at the metal/organic interface.

The existence of an interfacial layer, as suggested above and illustrated in Fig. 4, is consistent with the charge injection

efficiency observed in organic LEDs. The work function dependence manifests itself in the difference in the barrier height between the metal and the dipolar layer, rather than between the metal and the Alq layer. Thus for Mg/Alq and Au/Alq contacts, the barrier height is 0.76 and 2.2 eV, respectively. The lower barrier for the Mg contact is responsible for the more efficient electron injection into Alq. The importance of an interfacial layer in controlling the charge injection at metal/organic interfaces is also succinctly demonstrated in the following observations. The introduction of a thin (~ 0.5 nm) LiF or MgO layer between Al and Alq significantly enhanced the electron injection in OLED.¹⁹ On the other hand, the formation of a ~ 3 nm Ca oxide layer between the oligomer and the Ca metal prevented photoluminescence quenching due to metal induced midgap states.²⁰

In summary, the energy levels for Au/Alq and Mg/Alq interfaces have been determined by UPS measurements. The energy difference between the Fermi level and the HOMO edge of Alq is about 1.7 eV, which is the same for both high work-function Au and low work-function Mg. A Fermi level alignment model is proposed, assuming a charge transfer between the metal and Alq and the formation of a dipolar layer at the metal/Alq interface.

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