Distinguishing between interface dipoles and band bending at metal/tris-(8-hydroxyquinoline) aluminum interfaces

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Using a combination of photoelectron spectroscopies and ellipsometry to study the thin-film growth of Alq_3 (tris-(8-hydroxyquinoline) aluminum) on Ag, we have been able to distinguish between molecular orbital energy shifts due to ''band bending'' and interface dipole formation. We have observed large binding energy shifts (≈ 0.5 eV) of the organic molecular levels at low coverages. We conclude that these shifts are consistent with the formation of a polarized molecular layer, or interface dipole, and are inconsistent with an electrostatic band-bending model. © *2000 American Institute of Physics.* [S0003-6951(00)01538-2]

Molecular organic thin films have recently received renewed attention for their use in a wide variety of optoelectronic devices.[1] Despite the technological success of these devices, many of the electronic transport properties of these devices remain unknown.

In particular, much debate has arisen over whether or not ''band-bending''-like electrostatic energy shifts occur within these films. If, in fact, a depletion region is formed near a metalorganic interface, it must be taken into account when trying to analyze or simulate the current–voltage characteristics of an organic light-emitting device.

Surface scientists have played a great role in this debate. Several groups have asserted that band bending does not occur on length scales of ≈ 100 Å using ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS),[2–6] or on length scales of ≈ 1000 Å using the Kelvin probe technique.[7] These studies all identify an abrupt shift of the vacuum level at the metal/organic interface, due to strong polarization in the first molecular layer, which they interpret as an interface dipole.

Others, however, have proposed that most of the shifts seen at low coverages ($\leqslant 50$ Å) are in fact due to band bending.[8–11] Schlaf *et al.*[11] assert that the band-bending shift can be deduced from the shifts of the XPS atomic core levels, in the absence of strong chemical interactions at the interface, and that the true interface dipole shift is equal to the vacuum level shift minus the band-bending contribution. Of course, the presence of a depletion region implies the presence of ionized species, and therefore mobile carriers, which have been removed from the region which exhibits band bending.[12]

A careful study of these shifts, as a function of an accurately calibrated film thickness, would therefore be able to deduce the bulk density of mobile carriers required to produce the observed shifts. This density could then be compared with previously reported values of the density of free carriers in the material, derived from transport measurements, to determine whether or not the band-bending analy-

sis is appropriate. Additionally, the interface dipole model, which predicts that all shifts should occur within the first 1–2 molecular layers, could be more thoroughly tested using a more accurately calibrated film thickness.

In this letter we present our recent photoelectron spectroscopy studies of the early stages of the growth of a technologically important molecular organic material, Alq_3 (tris-(8-hydroxyquinoline) aluminum) on Ag. We have calibrated our film thickness using ellipsometry, which has allowed us to distinguish between electrostatic band-bending and interface dipole formation.

High purity Ag foils (99.99%, 0.2 mm thick, Sigma-Aldrich) were prepared in ultrahigh vacuum (UHV) by Ar ion sputtering. The cleanliness of the sputtered foils was estimated from their UPS and XPS spectra. Residual C contamination was estimated to be <1% of a monolayer. Alq_3 was purified by train sublimation, and deposited on the Ag substrates under UHV condition ($\approx 10^{-9}$ Torr) from resistively heated Al_2O_3 crucibles in a sample preparation chamber, and transported to the main analysis chamber (base pressure 5×10^{-11} Torr) without breaking vacuum. UPS studies were conducted using an Omicron Multiprobe system, consisting of a hemispherical electrostatic energy analyzer and a He discharge lamp. The overall energy resolution of the UPS system was ≈ 50 meV.

Deposition rates were estimated during the experiment using a quartz crystal microbalance, assuming an Alq_3 bulk density of 1.5 g cm^{-3}.[13] The thicknesses were later corrected by measuring the true thickness of a nominally 100 Å thick Alq_3 film on a flat Si(100) substrate using ellipsometry. The error in the film thickness has been estimated to be $\approx 10\%$, considering the uncertainty in this measurement due to the effects of varying unknown parameters, such as the dielectric constant of the Alq_3 film.

Figures 1(a) and 1(b) summarize the UPS measurements performed, as a function of Alq_3 thickness, for the Alq_3/Ag interface. The left panel (a) shows the onset of photoemission, which corresponds to the vacuum level of the surface, while the right panel (b) contains the portion of the spectrum around the metal Fermi level and Alq_3 highest occupied molecular orbital (HOMO). The metal Fermi level is observed at 19.9 eV, which is equal to the photon energy (21.22 eV),

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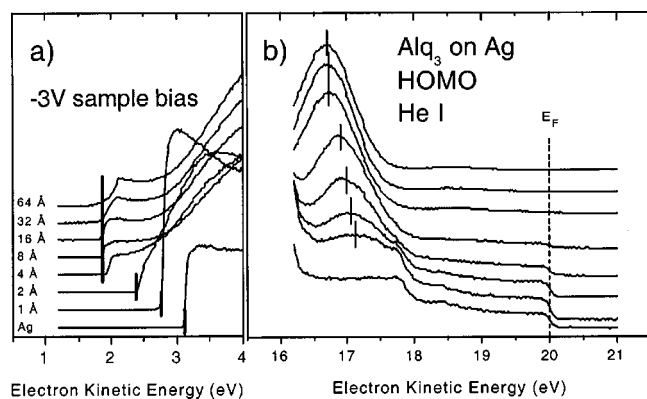
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FIG. 1. UPS spectra of Alq$_3$ deposited on Ag: (a) onset of photoemission, indicating the vacuum level of the surface; (b) spectral region around the Alq$_3$ HOMO. Tick marks are intended as a guide to the eye.

minus the work function of the analyzer (4.3 eV), plus the applied sample bias of 3 V. While the remainder of the spectra (4–16.5 eV) are certainly of general interest, they have been well documented elsewhere.[4,14] It suffices to mention here that our data are in excellent agreement with previously published results. The Alq$_3$ HOMO is clearly visible at the lowest coverage of 1 Å, and shifts to ≈ 0.5 eV higher binding energy with increasing film thickness. The Alq$_3$ HOMO energy remains constant for film thicknesses $\geqslant 16$ Å. We note that the metal Fermi edge is completely suppressed at a film thickness of $\leqslant 16$ Å, indicating that the metal surface is completely covered, consistent with the probing depth of the UPS technique (≈ 5 Å). The left panel clearly shows the abrupt shift of the vacuum level at low coverages. The onset of photoemission shifts to lower energy by >1 eV within the first 4 Å of coverage, and then remains constant within experimental uncertainty, up to a thickness of 64 Å.

Our observation of the abrupt shift in the vacuum level at the interface seems to support the interface dipole model,[2–6] but the more gradual, and lesser, shift of the Alq$_3$ HOMO level does resemble band bending as reported in previous studies.[8–11] However, as we shall explain in the following paragraph, the shift of the Alq$_3$ HOMO level cannot be due to band bending, and can be explained by the interface dipole model.
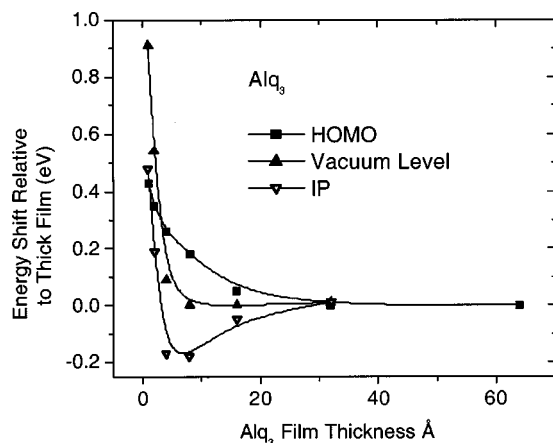
Figure 2 summarizes the observed shifts of both the

FIG. 2. Relative shifts of HOMO and vacuum levels of Alq$_3$, as well as the change in molecular IP as a function of overlayer coverage.

vacuum and HOMO levels as a function of Alq$_3$ film thickness. In addition, in Fig. 2 we have plotted the apparent change in the ionization potential (IP) of the Alq$_3$ film as the overlayer thickness increases.

We again note that the shift of the Alq$_3$ HOMO level does resemble traditional band bending. However, if we assume that these shifts are due to a net charge density within a depletion region, and use the magnitude of the shift and the thickness over which it occurs to calculate the mobile bulk carrier density required to produce such shifts, we arrive at a value of $\approx 10^{19}$–10^{20} cm^{-3}. An upper limit on the bulk carrier density in Alq$_3$ has previously been estimate to be 10^{12} cm^{-3}.[15] While there is certainly some uncertainty in each of these measurements, it is hard to reconcile a difference of 7–8 orders of magnitude.

To address the band-bending scenario further, we note that in the context of this model, energy levels, which shift as a result of this electrostatic effect are, by definition, a function of distance from the metal/organic interface. However the shifts, which we have observed, occur over a length scale of 15–20 Å, which is comparable to the dimensions of a single Alq$_3$ molecule, which has a radius of ≈ 10 Å.[16] When interpreting data from film thicknesses less than the dimensions of a single molecule, we must remember that as our apparent ''thickness'' increases, the film thickness does not. In fact, below this value it is the areal density of organic molecules that is increasing, and the distance from the metal/organic interface to the film surface (outermost organic ligands) remains, roughly, constant. It is therefore not appropriate to even consider band bending on these length scales.

We will now try to understand these results in the context of the interface dipole model. As noted previously, the abrupt shift of the vacuum level, which saturates at a coverage of 4 Å, is in excellent agreement with this model. It is the shift of the HOMO that we must try to understand.

It is well known that the IP of a molecule depends on the polarizability of its surroundings.[17–19] In fact, the IP of typical organic molecules in a solid film is ≈ 1.2–1.3 eV smaller than in the gas phase, due to the screening provided by neighboring molecules. Furthermore, it is to be expected that the IP of molecules in the first molecular layer should be smaller than in the bulk, due to the greater polarizability of the metal surface compared to the organic film. We therefore expect the following progression of observed IP as the deposition proceeds: (1) well below the completion of the first molecular layer, the IP should be greater than at the completion of the first layer, due to the absence of nearest neighbor molecules; (2) the IP should decrease, as the coverage increases, reaching a minimum at the completion of the first layer; and (3) the IP should then increase as the second layer forms and approach the bulk value. This is exactly what is observed in the experiment (Fig. 2). The relative HOMO and lowest unoccupied molecular orbital (LUMO) energies are illustrated in Fig. 3, assuming that the HOMO–LUMO splitting is equal to the optical absorption gap, and that the LUMO polarization shift is equal to that of the HOMO. These effects will be discussed in greater detail in a future publication,[20] in which we will describe our current UPS and XPS studies of related molecules (the 4-methyl Alq$_3$ derivative and Gaq$_3$).
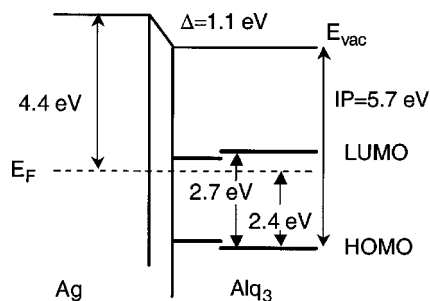
FIG. 3. Energy levels derived from the UPS studies. The energy levels are slightly offset (≈ 0.2 eV) in the first molecular layer (≈ 10 Å) due to the polarization screening of the metal surface.

We have shown that the organic energy level shifts observed at low coverages are not compatible with the band-bending model. This model predicts mobile carrier densities 7–8 orders of magnitude greater than those estimated by transport measurements. Furthermore, the length scale over which these shifts occur is comparable to the dimension of a single Alq_3 molecule, and it is therefore unphysical to consider energy levels that shift continuously over these distances.

The results can be completely understood in the context of the interface dipole model and the changes in polarization screening due to the metallic interface. We therefore conclude that there is no band bending and that a flatband condition occurs on these length scales.

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