

Initial stages of metal/organic semiconductor interface formation

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We have used photoelectron spectroscopies to study the metal/organic semiconductor interfaces formed by depositing three different metal–quinolate derivatives on Ag, with the goal of better understanding the initial stages of interface formation. We find very consistent results at all three interfaces, which exhibit strong energy level shifts within the first molecular layer, followed by a nearly “flat-band” condition. These results were analyzed in the context of the interface dipole and “band-bending” models. We conclude that the interface dipole model, extended to account for the differences in polarization screening in the first molecular layer, most accurately describes our findings. In this article we present the most thorough description of the early stages of metal/molecular organic semiconductor interfaces to date. © 2000 American Institute of Physics. [S0021-8979(00)02814-0]

I. INTRODUCTION

Organic semiconducting materials have now reached the early stages of commercialization, with organic-based small area electroluminescent displays being used in consumer electronic devices such as cellular phones. Despite the recent technological success of these materials, relatively little is understood about the charge injection and transport processes in organic semiconductor devices. A detailed understanding of the charge injecting interfaces is crucial to analyzing these processes.

Several research groups have used surface science techniques to study the formation of interfaces between metals and organic semiconductors, but a consensus on the analysis of these studies has yet to be reached. Two schools of thought have emerged which attempt to explain the energy alignment of the molecular orbitals with the Fermi energy of the substrate metal: interface dipoles and “band bending.”

The interface dipole scenario, in the context of metal/organic semiconductor interfaces, was originally proposed by Seki and co-workers,^{1,2} and has been supported by the work of others.^{3–7} In this model, a charged double layer exists at the interface. This effective separation of charge may be the result of any number of processes, including molecular polarization induced by the electronic image force, polar bond formation between the organic and the metal substrate, or charge transfer across the metal/organic interface. The double layer can be thought of as a parallel plate capacitor—an electric field exists between the plates, vanishes outside the plates, and results in a potential difference between the two plates. An interface dipole therefore results in an abrupt change in electrostatic potential energy at the interface. This energetic change manifests itself as an offset between the vacuum levels of the substrate metal and the organic molecular overlayer as measured by ultraviolet photoelectron spectroscopy (UPS). Prior to the findings of Seki and co-workers,

it was widely assumed that the vacuum levels would simply align, making the determination of charge injection barriers a simple matter of calculating the difference between the metal work function and the electron affinity or ionization potential (IP) of the organic solid.

The magnitude of the interface dipole is determined by measuring the surface vacuum level position as a function of organic overlayer thickness. The assumption is made that there is no band bending present, which would also shift the vacuum level. This assumption is normally justified by the small film thickness over which the shifts are observed (≈ 1 ML), and the extremely low conductivities of these materials, which imply an absence of free charge carriers. This assumption has been further justified by Seki *et al.*⁸ using Kelvin probe measurements to show that no detectable band bending occurs in ≈ 1000 Å layers of N',N' -diphenyl- N,N' -bis(3-methylphenyl)-1,1' biphenyl-4,4'-diamine (TPD) deposited on Au, Cu, Ag, Mg, and Ca.

There exists a great deal of misunderstanding, both in the organic surface science and organic semiconductor device communities, regarding the use of the term band bending. The term originates from the study of traditional crystalline inorganic semiconductors, where the characteristic energy levels of the occupied valence and unoccupied conduction states are described by delocalized wave functions. The shifting of these levels over some distance within the semiconductor is referred to as band bending.⁹ The origin of this effect, however, has nothing to do with the existence of delocalized states. Rather, it is purely an electrostatic effect, where the potential energy of a given state [conduction and valence bands; highest occupancy molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] becomes a function of position within a material, due to the presence of an electric field. Band bending usually refers to the situation where the mathematical form describing the energy levels as a function of position within the solid exhibits curvature. This curvature implies a net charge density present in the material, resulting in a nonzero second derivative of the electrostatic energy.⁹ It is therefore possible to

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estimate the net charge density from the measured curvature of the electrostatic shifts. Furthermore, because a net charge density can only result from the removal of charges from an initially neutral material, the curvature implies the presence of mobile carriers in the bulk, which have been swept from the volume which exhibits band bending. Given this definition, we wish to stress that although band bending may not be the most desirable of terms to describe shifts in organic molecular materials, it is, in fact, a reasonable phenomenon to discuss. However, one may question the validity of describing a molecular level "bending" over a length scale comparable to the dimensions of an individual molecule.

Despite the evidence presented by the groups of Seki and Kahn, others have proposed that the UPS data can be explained by band bending.¹⁰⁻¹³ Most notably, Schlaf *et al.*¹¹⁻¹³ have used x-ray photoelectron spectroscopy (XPS) analysis of atomic core levels, alone and in conjunction with UPS measurements of the valence structure and vacuum level, to measure energy shifts as a function of overlayer thickness. Their analysis does not preclude the existence of an interface dipole, but rather they assign a value to the band-bending energy (V_b) equal to the shifts of the XPS core levels. The magnitude of the interface dipole, they assert, is equal to the measured vacuum level shift, minus V_b . This analysis assumes that the atomic core levels shift rigidly with the valence features, such as the HOMO. The interpretation of core level shifts may be complicated by chemical interactions at the interface, resulting in shifts of the core levels, which may be mistaken for band bending.

The difficulty of determining the true film thickness complicates the analysis in either the interface dipole or band-bending scenarios. In the former model, one would like a reasonable estimate of the thickness at which the first molecular layer is complete, given that an interface dipole should form within the first layer. In the latter, the thickness over which a given energy shift occurs is used to estimate the required mobile carrier density. This density can then be compared with the measured transport characteristics of the material to test whether or not the results are physically reasonable. Unfortunately, as many of the organic thin films have not been well characterized, the thin film bulk density is typically unknown and must be estimated. In addition, the sticking coefficients for the organic molecules on the substrate metal films are also unknown. There is therefore a very large systematic error present in the experimental film thicknesses reported in the literature.

In this study, we have investigated the interfaces formed by depositing three metal chelate molecular films (Fig. 1): Gaq₃ [tris-(8-hydroxyquinolato) gallium], Alq₃ [tris-(8-hydroxyquinolato) aluminum], and Almq₃ [tris-(4-methyl-8-hydroxyquinolato) aluminum] on Ag. We have paid particular attention to the evolution of the molecular energy levels at low coverages in order to distinguish between band bending and interface dipoles. Finally, we have accurately calibrated our film thicknesses using ellipsometry.

II. EXPERIMENT

The substrates used in this study were Ag foils (99.99%, Sigma-Aldrich), which were prepared in ultrahigh vacuum

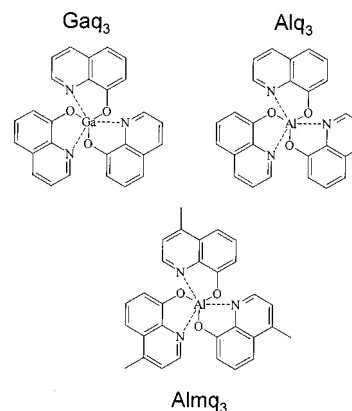


FIG. 1. Structures of the molecules used in this study.

(UHV) by Ar ion sputtering, and the cleanliness verified using XPS. The organic materials, purified by train sublimation, were deposited on these substrates under UHV conditions (typically 10^{-9} Torr) in a sample preparation chamber, which was connected to a main analysis chamber (base pressure 5×10^{-11} Torr) such that the samples were not exposed to air. UPS and XPS studies were conducted using an Omicron multiprobe system, utilizing a hemispherical electrostatic energy analyzer, a He discharge lamp, and a Specs double anode (Mg and Al) x-ray source. The overall energy resolution was determined to be ≈ 50 meV for UPS, and ≈ 1 eV in XPS, which in practice was limited by the Al $K\alpha$ line width at low pass energies, and by the analyzer resolution at higher pass energies.

During the experiment, the film thicknesses were estimated using a quartz crystal microbalance, assuming a bulk density of 1.5 g cm^{-3} , which has been reported for thin films of Alq₃.¹⁴ These thicknesses were later calibrated by depositing nominally 100 Å thick films on flat Si(100)/native oxide substrates, and measuring the actual thickness using ellipsometry. Using this method, we have estimated our experimental film thickness error to be $\approx 10\%$, considering the uncertainty in the ellipsometry measurements, the scatter in results taken at various locations on the same sample, and the effect of varying unknown parameters, such as the dielectric constant of the quinolate films.

III. RESULTS

XPS core level peak positions, and UPS HOMO peak positions were determined by nonlinear least squares fitting of Gaussians to the data after appropriate background subtraction. For XPS, the background was assumed to be of the Shirley form, which accounts for inelastic electron scattering, and for UPS a polynomial fit to the background on either side of the peak was used. Gaussian peaks were used, in the case of XPS, due to the instrumental resolution limited nature of the measurement. In UPS, the nature of the HOMO derived density of states in these disordered films has been previously modeled as the superposition of individual molecular states with slightly varying binding energies, due to disorder, which appear as a normal distribution about a mean binding energy.¹⁵

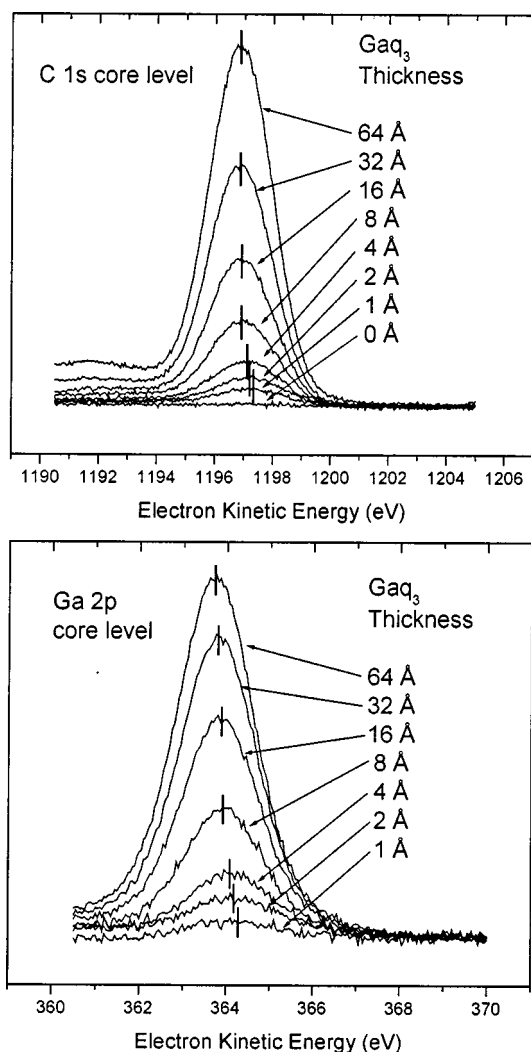


FIG. 2. XPS core levels measured during the formation of the Gaq_3/Ag interface. (a) C $1s$ core level. (b) Ga $2p$ core level. Vertical lines are intended as a guide to the eye. Actual peak positions were determined using peak fitting routines.

Gaq_3 was chosen for XPS studies, as the photoionization cross section of Ga at the photon energies available is much greater than that of Al, allowing accurate measurements of the metal core level energies at much lower coverages than would be possible with Alq_3 . The measured C $1s$ and Ga $2p$ core levels are presented in Fig. 2. Both core levels are clearly visible at the lowest film thickness of 1 Å, and appear to shift to lower kinetic energy (higher binding energy) with increasing thickness, as has been previously reported.¹² The uncertainty in the binding energies is of the order of 100 meV, and the shifts of the Ga and C core levels appear to be equal, within experimental uncertainty, implying a rigid shift of the core level binding energies with increasing coverage. This implies that the electron distributions around the Ga and C atoms do not change appreciably with increasing coverage.

Alq_3 and Almq_3 were studied using UPS. Examples of the UPS data for Alq_3 and Almq_3 deposited on Ag are shown in Figs. 3 and 4, respectively. In both cases, the organic HOMO is visible at the lowest coverage of 1 Å, and appears to shift to higher binding energy with increasing coverage,

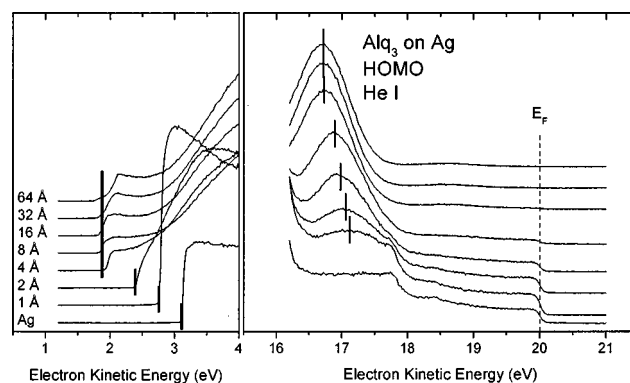


FIG. 3. UPS spectra of Alq_3 deposited on Ag. (a) onset of photoemission, indicating the vacuum level of the surface. (b) spectral region around the Alq_3 HOMO. Tick marks are intended as a guide to the eye.

following much the same pattern as the atomic core levels of Gaq_3 . Included in Figs. 3 and 4 are the low energy onsets of photoemission, which indicate the vacuum levels of the surfaces. The UPS data also indicate that the first molecular layer is completely formed prior to a film thickness of ≈ 16 Å, given the approximate probing depth of 5 Å, and the fact that the substrate Ag features and Fermi level are completely suppressed at this coverage. The nominal thickness of the first molecular layer can be estimated to be ≈ 10 Å given the measured bulk density and the molecular mass of the quinoxalines. It is interesting to note that the diameter of a sphere which would enclose a single Alq_3 molecule is ≈ 20 Å,¹⁶ implying that the molecules are significantly interdigitated in the bulk film.

Upon first inspection, we note that although the direction of the vacuum level shifts in Figs. 3 and 4, as well as the length scale over which the shifts occur, appear to be consistent with the observed HOMO shifts, the magnitudes of the shifts differ considerably. While the reason for this discrepancy is not immediately evident, it is, in fact, essential to the analysis and will be discussed in detail in the next section.

IV. DISCUSSION

We will first discuss the core level shifts observed at the Ag/Gaq_3 interface, and the HOMO shifts at the

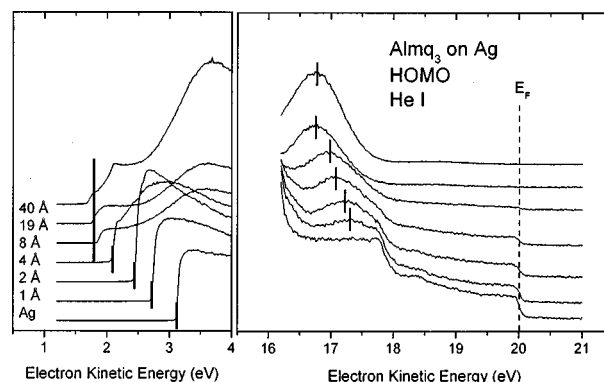


FIG. 4. As in Fig. 3, for Almq_3 deposited on Ag.

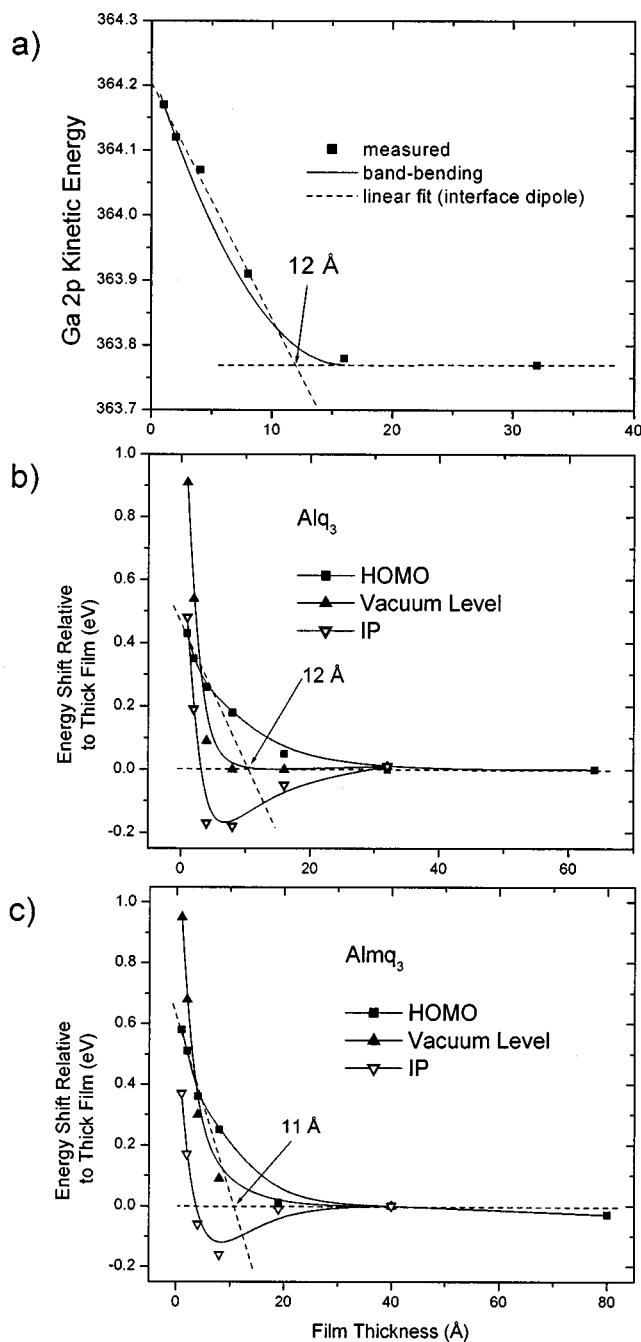


FIG. 5. Relative shifts of XPS core levels [panel (a) Ga₂p] and HOMO and vacuum levels [panels (b) Alq₃, (c) Almq₃]. Panel (a) includes a quadratic fit to the data, applicable to a band-bending analysis, as well as an estimate of the thickness corresponding to the completion of the first molecular layer in the interface dipole model. (b) and (c) also indicate the change in molecular IP as a function of overlay coverage.

Ag/(Alq₃ or Almq₃) interfaces. The relative positions of the Ga 2*p* core levels are presented in Fig. 5(a). We will now proceed to analyze the core levels shifts in terms of the two proposed models—band bending and interface dipole formation.

Using the simple depletion approximation⁹ we assume that the depletion region (where the band bending occurs) contains a constant net charge density due to ionized impurities and the absence of free carriers, which have been swept from the region by the resulting electric field. The energy

levels should be described by a simple quadratic polynomial. Outside the depletion region, the net charge density is zero, and the levels are constant. A quadratic fit to the core levels is shown in Fig. 5(a). This fit results in a depletion width of ≈ 16 Å, which would require an ionized impurity concentration (and therefore a free carrier concentration in the bulk) of $\approx 5 \times 10^{19} \text{ cm}^{-3}$. This is clearly unreasonable given the upper limit of 10^{12} cm^{-3} which has been placed on the free carrier density in bulk Alq₃ by transport measurements.¹⁷ In addition to the unreasonable carrier concentration required to produce band bending, one cannot describe the molecular energy levels as shifting continuously on this length scale, given the effective diameter of a single quinolate molecule (≈ 20 Å). Band bending, by definition, describes the shifts of energy levels as a function of position in, or thickness of, a film. Below the monolayer coverage (≈ 10 Å), the thickness of the film does not actually increase with increasing deposition. Rather, it is the molecular areal density on the surface which increases. Shifts observed during the deposition of the first molecular layer cannot, by definition, be described as band bending. We therefore conclude that the observed shifts are not due to simple electrostatic band bending.

We will now consider these shifts in the context of the formation of an interface dipole. First, we assume that an organic molecule placed on a clean metal surface will be polarized, perhaps by the electronic image force just outside the surface.^{1,2,4,5} The image force decays as $1/r^2$, where r is the distance from the metal surface. We will therefore assume, in the first approximation, that only the first molecular layer will be polarized. We will also assume that the individual dipoles do not interact. The latter assumption is clearly valid at low coverages, where the intermolecular distances are relatively large. As noted previously, the first molecular layer will be completed at a nominal coverage of ≈ 10 Å, so the lowest coverages examined here should be well described by this approximation.

The presence of polarized molecules on the surface of the metal will produce a localized electric field, shifting the surface vacuum level to lower energy, facilitating the escape of electrons from the surface. The magnitude of the vacuum level shift (interface dipole) will be proportional to the areal density of polarized molecules,¹⁸ and therefore the vacuum level shift should be linear with the molecular coverage (nominal thickness) at low coverages. If the IP of the molecules is not significantly altered by the polarization, the atomic core levels should shift rigidly with the vacuum level. Within our above assumptions, we would predict these shifts to continue until the first molecular layer is complete, and that the levels should remain constant after its completion. The linear fits included in Figs. 5(a)–5(c) illustrate such a scenario. The intersection of the low-coverage and high-coverage fits should occur at a thickness corresponding to the completion of the first molecular layer. We note that the monolayer thicknesses estimated using this procedure (12 ± 1.2 , 12 ± 1.2 , and 11 ± 1.1 Å) are in reasonable agreement with the expected thickness of ≈ 10 Å, despite the simplifying assumptions outlined above. We note here an important distinction between the band bending and dipole scenarios: While band bending describes a continuous shift of the en-

ergy levels with distance through the depletion region (unreasonable given the relative sizes of the resulting depletion region and a single quinolate molecule), the interface dipole described above results in *all* molecular levels shifting together as the first monolayer is completed. The energy levels observed after the first layer is completed are therefore the values used to describe charge injection barriers.

We will now discuss in detail the relationship between the vacuum level shifts and HOMO shifts observed in the UPS studies of Alq₃ and Almq₃. Figures 5(b)–5(c) include the vacuum level positions relative to their high-coverage values. We note that the vacuum level shifts are larger, and occur over a shorter distance than the observed HOMO shifts. At first this seems to contradict the description of the formation of the interface dipole outlined above, where we assumed that the vacuum level and the molecular energy levels should shift rigidly. This was based on the assumption that the molecular IP is constant. We will now abandon this assumption, and note that the change in the molecular IP is equal to the difference between the relative vacuum level and HOMO positions in Figs. 5(b)–5(c). This difference is also included in the figure. The experiment illustrates that the first molecules deposited on the surface appear to have a higher IP than those at the surface of a bulk organic film (high coverage values). As the coverage is increased, the IP of *all* of the surface molecules decreases, reaching a minimum value, after which the IP increases and approaches that of molecules at the surface of the organic film.

To understand the above changes in the molecular IP, we must consider the IP of gas phase molecules, how, and why the IP is affected when a condensed film of the molecules is formed. In the condensed phase we must also consider the effect of the surface (as opposed to the bulk) on the molecular IP.

For a vast number of organic molecules, the molecular IP has been found to be ≈ 1.2 eV less in a condensed film than in the gas phase.¹⁹ This decrease in IP is due to solid-state electronic polarization of the surrounding film, which screens the hole resulting from the removal of an electron from a single molecule. The difference between the gas phase and solid state IPs increases with the polarizability of the surrounding medium. At the surface of an organic molecular film, the IP is slightly higher than it is in the bulk, due to the decreased coordination of the surface molecules. Typically, the difference between the thin film bulk and surface IPs is ≈ 0.2 – 0.3 eV.^{20,21}

We must now consider how the physisorption of a single organic molecule on a metallic surface affects the molecular IP. To do so, we will follow the procedure outlined by Harrison²² to describe the change in IP of an O atom adsorbed on a metal surface. We first consider the quinolate molecule and metal surface to be separated sufficiently such that the molecule can be described as being in the gas phase. We now imagine removing an electron from the HOMO, and moving it an infinite distance from both the molecule and the metal surface. This requires, by definition, an energy equal to the gas phase IP. We now allow the molecular cation to move towards the surface. In doing so, it will experience an attractive force due to the electrostatic image force and will

therefore lose potential energy. When the molecular cation comes to rest on the surface, the change in potential energy can be calculated as $e^2/4r$, where r is the estimated distance of the positive charge from the metal surface. If we now consider a neutral molecule on the surface, we will require an energy equal to the gas phase IP *minus* the above change in potential energy in order to remove an electron from the HOMO to infinity. This value is then the IP of a single molecule adsorbed on a metal surface. For a quinolate molecule (diameter ≈ 20 Å), and given that in UPS we are most sensitive to electrons photoexcited from the quinolate ligands farthest from the metal surface (given the finite probing depth of ≈ 5 Å), we estimate the photohole–metal surface distance to be ≈ 10 Å, predicting the molecular IP to be ≈ 0.4 eV smaller than the gas phase value. This implies that the IP of a single, isolated, quinolate molecule on a metal surface is ≈ 0.6 eV *larger* than a molecule at the surface of a quinolate film. While this result may seem surprising, given the much higher polarizability of the metal surface compared to the molecular film, it is a result of the much lower coordination of the isolated adsorbed molecule. Thus, we can rationalize the experimental observation of an increased molecular IP at low coverages.

As the quinolate coverage is increased, but remains sub-monolayer, the polarization screening will increase, as an individual molecule begins to be affected by the increasing number of nearest neighbor molecules on the surface. Thus, we expect that the molecular IP will decrease from the single adsorbate value as the first molecular layer is formed. We also predict that the IP should reach a minimum value at the completion of the first monolayer, as the polarizability of the metal surface is greater than that of a plane of molecules. As the second molecular layer forms, we predict that the IP of the outermost molecules should increase and approach the organic film surface value as the surface molecules are no longer affected by the subsurface metal interface. This is precisely what is observed in the experiment.

We can estimate the depth of the IP minimum as follows. We assume, given the probing depth of UPS (≈ 5 Å) and the size of the quinolate molecules (≈ 20 Å), that we are predominantly sensitive to the surface molecules at each film thickness. In Figs. 6 and 7 we present six different environments for a single molecule, and the resulting HOMO level shifts due to differences in polarization screening, respectively. We have previously estimated the following differences in IP: The gas phase (1) and isolated adsorbate (2) differ by ≈ 0.4 eV, the gas phase (1) and the bulk film (5) differ by ≈ 1.2 eV, and the gas phase (1) and the surface of the film (6) differ by ≈ 1.0 eV. In Fig. 6, environment 5, we have labeled three regions which surround a single molecule: a, b, and c. From the above estimates, we conclude that the polarization due to regions a and c are ≈ 0.2 eV each, and region b contributes ≈ 0.8 eV. The minimum IP occurs at the completion of the first molecular layer (3), and the total polarization energy is ≈ 0.4 eV (metal surface) + 0.8 eV (region b) = 1.2 eV. This implies that the IP of the monolayer (3) should be ≈ 0.2 eV smaller than that of the bulk surface (6). This is in excellent agreement with the measured IP minima [Figs. 5(b)–5(c)]. We also note that once

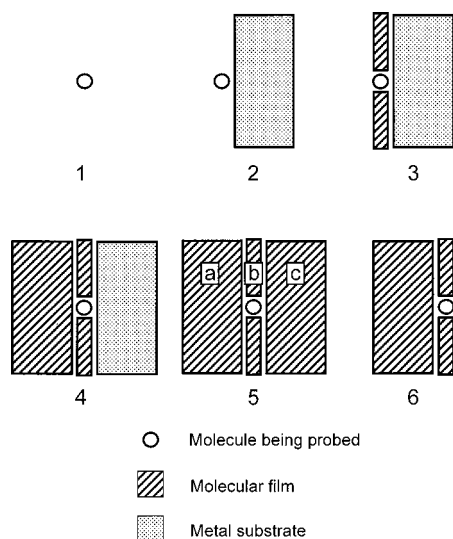


FIG. 6. Different environments for a single molecule: (1) molecule in gas phase, (2) isolated molecule on a metal surface, (3) one complete molecular layer on a metal surface, (4) first molecular layer on metal surface, beneath a molecular film, (5) bulk molecular film, away from both the metal interface and the film surface, and (6) surface of a molecular film.

the first molecular layer on the metal surface is buried (4), the IP of the first molecular layer will be further reduced by ≈ 0.2 eV, due to the screening of the overlayer. We would like to stress that the values given for the polarization energies are approximate, and are only provided to justify the above arguments.

Given the above analysis, we suggest that the most appropriate method of determining the film thickness corresponding to the completion of the first molecular layer is from the coverage at the minimum observed IP. The IP minimum is found at 8 ± 2 Å at both the Ag/Alq₃ and Ag/Almq₃ interfaces. Using the reported bulk density of Alq₃,¹⁴ and assuming that the molecular density in the first molecular layer is equal to that in the bulk, the nominal coverage corresponding to the completion of the first molecular layer is 8 Å, in excellent agreement with the IP minima positions.

In Fig. 8 we present molecular energy level diagrams for the Ag/Alq₃ and Ag/Almq₃ interfaces. The figure indicates the UPS measured values of the interface dipole, Δ (1.1 eV and 1.2 eV), and the binding energy, relative to the Fermi level,

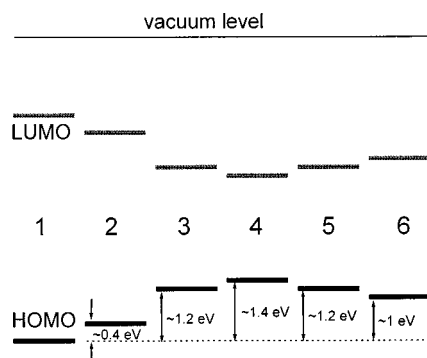


FIG. 7. Changes in HOMO and LUMO levels depending on the molecular environments in Fig. 6. The UPS measurements presented here have studied the HOMO in environments (2), (3) and (6).

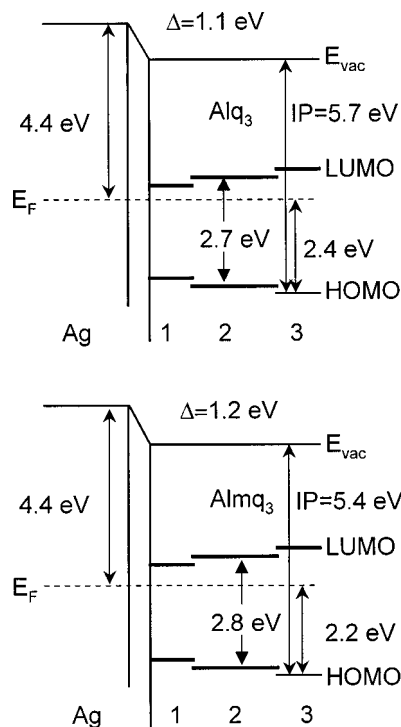


FIG. 8. Energy levels derived from the UPS studies. (a) Alq₃ interface. 2.35 eV is the difference in energy between the metal Fermi level and the low binding energy edge of the HOMO derived peak at the surface of the thick film. Regions 1, 2, and 3 represent the first molecular layer, the bulk film, and the surface, respectively. The HOMO/LUMO discontinuities at 1, 2, and 3 are ≈ 0.2 eV. (b) as above, for Almq₃.

of the low binding energy edge of the HOMO derived peak at the surface of the organic film (2.4 and 2.2 eV). Three regions within each organic film have been identified: The first molecular layer (1), the bulk of the film (2), and the surface (3). The discontinuities between the HOMO and LUMO levels between these regions are due to the differences in polarization screening, and are ≈ 0.2 eV. The LUMO positions have not been measured, but rather have been estimated using the measured optical gaps of 2.7 eV. Note that the optical absorption gap is a bulk, and not a surface or interface property. This estimate of the LUMO level ignores excitonic effects, and the true LUMO levels are probably farther above the Fermi level than indicated here.

V. CONCLUSION

We have used x-ray and ultraviolet photoelectron spectroscopies to study the organic/metal interfaces formed by depositing Gaq₃, Alq₃, and Almq₃ on Ag. We have analyzed the molecular and vacuum level shifts observed at low coverages in terms of two proposed models: band bending and interface dipoles. Although the observed shifts resemble band bending, we have found that the band-bending analysis is unphysical, because of the length scales involved compared to the size of an individual molecule, and because of the large density of free carriers implied by the analysis. Instead, we have found the results to be in complete agree-

ment with the formation of a layer of polarized molecules at the metal–organic interface, resulting in an interface dipole.

Furthermore, through the relative shifts of the vacuum and molecular levels we have gained a great deal of insight into the formation of the dipolar layer, and the evolution of solid-state screening effects. We have presented a complete and consistent description of the evolution of these energy levels during the formation of the first few molecular layers. We believe this to be the most comprehensive and detailed description of a metal–organic molecular thin film interface to date.

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