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Organic Electronics 2 (2001) 89–95

Organic Electronics

www.elsevier.com/locate/orgel

The role of interface states in controlling the electronic structure of Alq_3/reactive metal contacts

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Received 8 May 2001; received in revised form 22 June 2001; accepted 25 June 2001

Abstract

Gap states induced by the formation of metal/organic interfaces have been observed in a number of instances. Yet, the role that these states play in determining the electronic structure of the interface and the carrier injection barriers has not been clearly established. In this paper, we provide a model for the role of chemistry-induced gap states at Mg/Alq_3 and Al/Alq_3 interfaces, in particular with regard to the formation of dipole barrier and level bending. We show that these states play a defining role in producing identical Fermi level positions at metal-on-organic and organic-on-metal interfaces. The model is supported by photoemission and current–voltage measurements. © 2001 Published by Elsevier Science B.V.

Keywords: Interface states; Molecular film; Metal–organic interface

1. Introduction

Electronic structure [1–6], chemical reactions [7–12] and interdiffusion [11,12] have been investigated at a number of interfaces between metals and π-conjugated molecular films over the past few years. The alignment of molecular levels across the interface is found to depend on the respective electronic structures (e.g. work function, electron affinity (EA) and ionization energy (IE)) and chemical interactions between these materials. Many of the metal–organic interfaces investigated to date exhibit a large (~0.5–1 eV) dipole barrier [13] corresponding to a discontinuity in the vacuum level across the interface. Understanding the origin(s) of the dipole is important for achieving fundamental understanding of metal/organic interfaces and accurate description of the charge injection process across these interfaces.

Interface dipole barriers are expected to be present, and their origin well understood, in the following cases. First, the metal work function is smaller than, or equal to, the EA of the organic material (Fig. 1(a)). Upon interface formation, and assuming no further interaction, the Fermi level of the metal (E_{FM}) is above or at the lowest unoccupied molecular orbital (LUMO) of the organic film, leading to charge transfer across the interface. The electron transfer from the metal to the LUMO of the interface molecules raises the potential energy of the organic film and stops the

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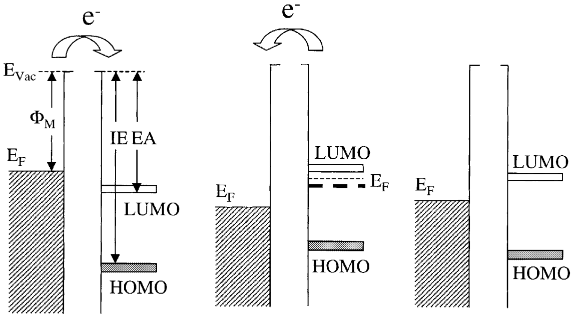
PII: S1566-1199(01)00015-5



(a) (b) (c)

Fig. 1. Scenarios for three different types of metal/organic interfaces: (a) the metal work function is smaller than the organic EA, inducing a electron transfer from the metal to the organic film; (b) the organic Fermi level is pinned, inducing an electron transfer to the metal to align the Fermi levels; (c) the metal work function is between the organic EA and IE, and the Fermi level is not pinned in the organic film.

charge transfer. This charge transfer establishes a *negative* interface dipole (sign chosen by convention). This situation is encountered at interfaces between low work function metals and organic materials that have large EA (• 4 eV), e.g. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) deposited on In or Mg [3], and 3,4,9,10-perylenetetracarboxylic bisimidazole (PTCBI) deposited on Mg or Ag [14]. Note that in these cases, photoemission spectroscopy clearly points to the localization of the charge on the first or second molecular plane, consistent with an abrupt dipole barrier. No level bending away from the interface is observed in these specific cases. In the second case, the metal work function is larger than the organic EA and smaller than the IE, but the Fermi level of the organic film (E_{FO}) is "pinned" in the bulk as well as at the surface by defects or impurities (Fig. 1(b)). This situation is observed with large work function metals-like Au in contact with PTCDA or PTCBI, which consistently exhibit "n-type" behavior with the Fermi level pinned near the LUMO. Note that this n-type behavior is obtained in spite of the extensive purification procedure used for all these organic materials (triple sublimation cycle under temperature gradient). Upon formation of the interface, electrons are transferred from the organic film to the metal to align the two Fermi levels, inducing a *positive* dipole [3,14].

The interfaces studied here, i.e. Mg-(Al-)Alq$_3$ (tris-(8-hydroxy quinoline) aluminum) are more complex and do not fall in either of these two categories. The IE and EA of Alq$_3$ (as determined by direct and inverse photoemission spectroscopy) are 5.9 and 2.1 eV [15], respectively, and bracket the work functions of both Mg (3.7 eV) and Al (4.2 eV) (Fig. 1(c)). Alq$_3$ is also more "intrinsic" than the materials above. Photoemission spectroscopy shows that E_{FO} is near mid-gap in pristine Alq$_3$, and relatively free to move upon formation of an interface with a metal [13]. Short of considering an interface interaction that determines a specific alignment of the molecular levels with respect to E_{FM}, one could therefore expect an interface with little if any charge exchange and dipole barrier. However, experiments clearly show that both interfaces exhibit a 0.8–1 eV positive dipole barrier, consistent with an electron transfer from Alq$_3$ to the metal. This result is clearly counter-intuitive, given the low density of free carriers in the intrinsic material and the low work function of the metal.

We show in this paper that interface gap states play a decisive role with regard to this issue. Ultraviolet photoemission spectroscopy (UPS) studies of the formation of interfaces between low work function metals and Alq$_3$ have pointed out in several instances the presence of filled interface gap states above the highest occupied molecular orbital (HOMO) of the organic materials [4,8,12]. The interaction between Ca, K and Na and Alq$_3$ consists in the formation of anion–cation pairs [4,8,12]. The gap states presumably correspond to the occupation of the LUMO of the molecule by charge transferred from the metal atom. The charge induces relaxation of the electronic structure of the molecular ion, leading to filled states deep into the gap. In the case of Al and Mg, the chemical interaction is different, involving covalent metal–carbon bonds that result in the formation of organo-metallic complexes [10]. UPS data recorded for Al and Mg deposited on Alq$_3$ show a drastic disruption of the valence states with respect to those of the pristine molecule. We reported three years ago the formation of gap states ~1.8 eV above the Alq$_3$ HOMO upon deposition of Mg

[1]. We recently reported the formation of similar states for Al as well as for the reverse deposition sequence with both metals [12], consistent with the similar chemistry reported at the two types of interface.

In spite of the ubiquitous presence of gap states at a number of important metal–organic interfaces, their role in the interface energy level alignment and charge injection process remains to be clarified. In particular, whether the gap states are the result of charge transfer induced by a primary mechanism that sets up the dipole barrier, or whether they constitute the driving force behind the dipole barrier is yet unclear. The present paper addresses this issue. We extend the interpretation of previously published data [10,12] to show that, in the case of the Mg-(Al-)Alq_3 interfaces, the exothermic metal–molecule chemistry is the driving force behind the re-alignment of the molecular levels and the interface dipole barrier.

2. Experiment

All experiments are performed in interconnected growth and analysis ultra-high vacuum chambers. Mg, Al and Alq_3 are deposited by thermal evaporation in the growth chamber at a base pressure below 1×10^{-9} Torr. The basic substrate consists of a pre-prepared Au (500 Å)/Cr (250 Å)/Si wafer. For studies of organic-on-metal interfaces, a 500 Å thick metal layer is first deposited in situ on the wafer, then the organic layer is incrementally deposited on that metal layer at a rate of 0.2–0.5 Å/s. Conversely, the studies of metal-on-organic interfaces are done by incremental deposition of metal at a rate of 0.2–0.5 Å/s on a 100 Å thick organic film deposited on the wafer. Following each deposition, the sample is transferred to the analysis chamber for analysis of interface electronic structure, i.e. interface molecular level positions and dipole barriers as a function of interface formation, via UPS. The resolution of the UPS measurements, performed with a He discharge lamp and a double-pass cylindrical mirror analyzer, is 0.15 eV. The analysis of substrate cleanliness and interface chemistry is done via X-ray photoemission spectroscopy (XPS). The details of the chemical analysis on Mg/Alq_3 and Al/Alq_3 interfaces have been reported elsewhere [13].

3. Results and discussion

The exothermic reaction between Mg or Al and Alq_3 derives from the tendency of these two metals to form strong covalent bonds with carbon. According to our previously published model [10,12], the metal atom reacts at the pyridyl ring of the quinolate ligand and is oxidized by donation of charge to the Alq_3 LUMO, which is maximized on the pyridyl ring and at N. The appearance of a reacted component of the Mg(2p) (Fig. 2) and Al(2p) core levels, shifted toward higher binding

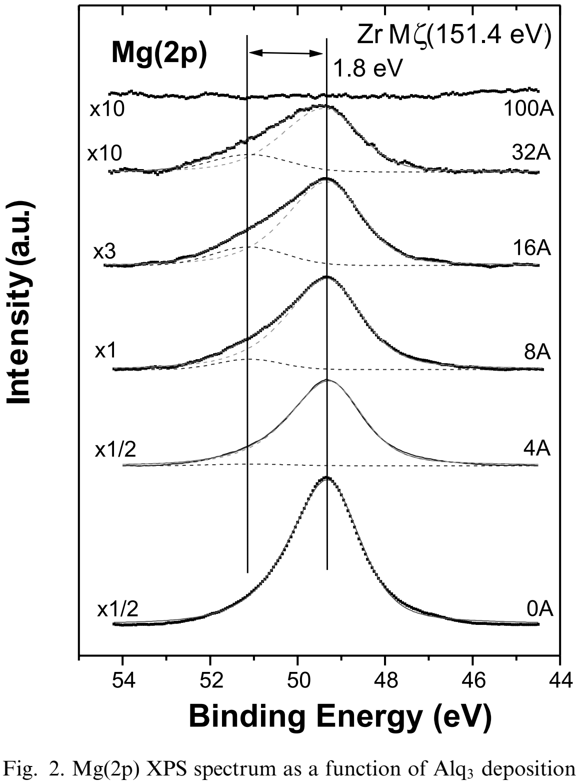


Fig. 2. Mg(2p) XPS spectrum as a function of Alq_3 deposition on Mg. The high binding energy component indicates that the Mg surface is oxidized (loses charge to Alq_3). The peak area decays exponentially as a function of Alq_3 coverage, indicative of homogeneous coverage and interface abruptness.

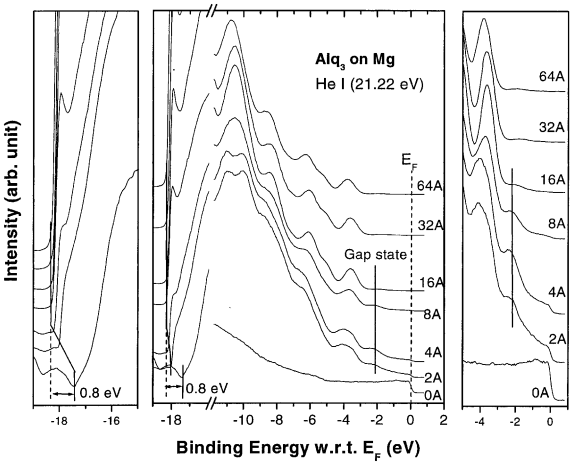


Fig. 3. UPS spectra as a function of Alq_3 deposition on Mg, showing the photoemission onset (left), the full valence states (center), the HOMO and band gap region (right). The vertical full lines indicate the interface gap states.

energy with respect to the metallic component, clearly indicates this partial electronic charge transfer. The resulting negative charge buildup on the ligand, along with some rehybridization at N from sp^2 to sp^3, results in a lowering of the binding energy of the N(1s) core level. The metal atom also coordinates to a quinolate oxygen atom, which reduces the donor ability of that oxygen with regard to the central Al atom of the Alq_3 molecule, resulting in the increase in the binding energy of the O(1s) and Al(2p) core levels reported by our group [10,12].

Fig. 3 shows the full He I UPS spectrum of Alq_3 (center), the photoemission onset (left) and the HOMO region (right) as a function of Alq_3 deposition on Mg [12]. The center and right-hand panels clearly show the presence of filled states in the gap of Alq_3, ~1.8 eV above the HOMO. The intensity of these states reaches a maximum below one molecular layer (4–8 Å), demonstrating confinement of the states to the interface. This is consistent with the fact that the UPS spectrum (center panel) rapidly evolves with coverage and assumes the line shape characteristic of the electronic properties of pristine Alq_3. It is also consistent with the XPS data, which show confinement of the chemical reaction to the interface region [12]. The slight shift of the UPS spectrum to higher binding energy at 64 Å is presumably due to photoemission-induced charging effect because of the extremely low hole mobility of Alq_3 film. The shift of the photoemission onset toward lower energy (left panel) indicates a step-down of the vacuum level from the metal to the organic film, consistent with a positive dipole (as defined above), and in apparent contradiction with the direction of the metal–molecule charge exchange. As a side note, the abruptness of the interface region is to be contrasted with the result of the reverse deposition sequence (metal-on-Alq_3), which leads to considerably broader interfaces with reacted species several molecular planes below the interface front [12].

The contradiction mentioned above is resolved by considering the role played by the *chemistry-induced* interface states. On another reactive system, i.e. In/PTCDA, our group has reported a large density of gap states seen in UPS [11]. These states were later associated by Kera et al. [16] with the HOMO and HOMO−1 of the In_4–PTCDA organo-metallic complex resulting from the metal–molecule reaction. A theoretical investigation performed by the same group [16] and inverse photoemission spectroscopy (IPES) measurements done in our laboratory [17] further show that these gap states are derived from the original LUMO and LUMO+1 of the PTCDA molecule, now occupied by electronic charges transferred from In. UPS and IPES studies of K deposited on C_{60} also show that gap states above the HOMO originate from the occupation of LUMO by charge transfer from the alkali atom [18]. We suggest a similar origin for the gap states observed at the Mg-Alq_3 and Al-Alq_3 interfaces, although the IPES measurements and theoretical calculations remain to be done.

Fig. 4 illustrates the proposed model for the formation of the dipole barrier. Following deposition of Alq_3 on the metal substrate (a), the exothermic chemical reaction and metal atom–molecule charge transfer take place (b), leading to the formation of an organo-metallic complex and associated filled gap states. The complex is neutral regardless of the charge redistribution between Mg and Alq_3. Since the gap states are filled, the Fermi level, which is located near mid-gap in the

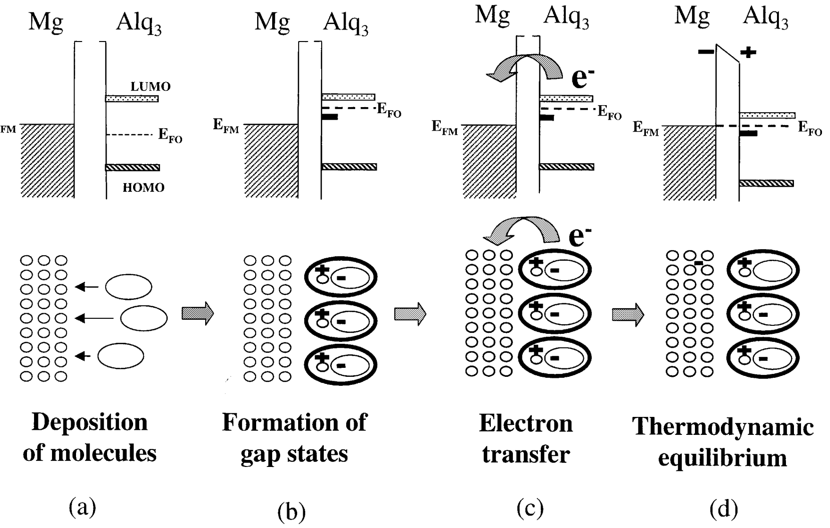


Fig. 4. Formation of a dipole induced by charge exchange between the organo-metallic complex and the metal: (a) organic molecules are initially deposited on metal; (b) chemical reaction and charge redistribution between surface metal atoms and organic molecules, formation of gap states, and Fermi level (E_{FO}) pinning between gap states and LUMO; (c) electron transfer from the organo-metallic complex to the metal; (d) thermodynamic equilibrium, with Fermi level alignment and interface dipole.

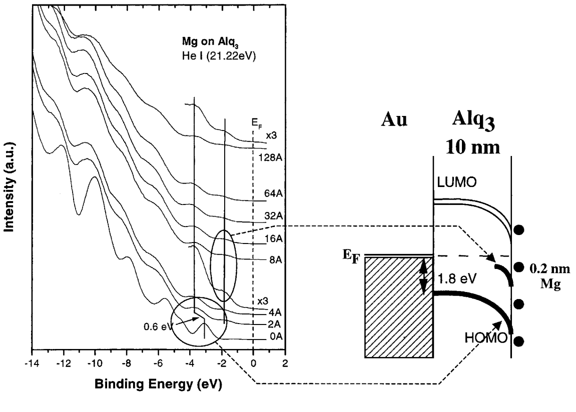
undoped and pristine organic material, is pushed upward between the gap states and the LUMO level (b). The misalignment between the two Fermi levels leads to an electron transfer from the complex molecules to the metal (c), until thermodynamic equilibrium is established, generating a positive dipole (d).

The above argument does not rely on the specific origin of the gap states. The driving force in the Mg-Alq_3 and Al-Alq_3 systems is the exothermic chemical reaction. However, other mechanisms are possible. In systems where the interaction is limited to cation–anion pair formation, like Ca, Li or K on Alq_3, Fermi level pinning in the upper part of the gap due to filled states occurs as well. The IE of Ca and of most alkali metal atoms is of the order of 4–6 eV. When deposited on and diffused into the organic film, the isolated metal atom is stabilized by surrounding molecules, its IE decreased by polarization, and its highest occupied level raised close to or higher than the organic LUMO. This leads to charge transfer without the formation of covalent bond. Relaxation and polarization stabilize the newly occupied level, or polaron, which is detected as a gap state.

The gap states provide the charge required to establish thermodynamic equilibrium between the metal and the organic material. Assuming a 10 Å metal–molecule distance and a dielectric constant $\varepsilon = 3$, the interface charge density n_{int} can be extracted using Gauss's law, $n_{\mathrm{int}}/\varepsilon = E$, where E is the electric field. The field is estimated to be 0.8 V/10 Å at the Alq_3/Mg interface, leading to a charge density of 1.3×10^{13} e/cm^2. Equating the density of interface Alq_3 molecules of 10^{14} cm^{-2} to the density of gap states, assuming that each Alq_3 molecule undergoes chemical reaction, one obtains that a uniform distribution of only 13% of the gap states need to be ionized to sustain the observed dipole. All other states remain occupied, and thus detectable via UPS.

Fermi level pinning by gap states is observed at both Mg(Al)-on-Alq_3 and Alq_3-on-Mg(Al) interfaces, regardless of the different interface morphologies. In the case of organic-on-metal, metal atoms diffuse little, if any, into the organic film and the metal–molecule interaction is essentially limited to the first molecular layer. At the metal-on-organic interface, the penetration of metal atoms to subsurface molecular planes leads to an extended interfacial region. However, E_{FO} is pinned at nearly identical positions at both interfaces due to the formation of similar chemistry-induced states [12]. Similar energy alignments at organic-on-metal and metal-on-organic interfaces result in symmetric carrier injection, as demonstrated by symmetric current–voltage characteristics recorded for metal/Alq_3/metal sandwich structures (metal = Al, Mg) [12]. In contrast, interfaces where no gap states exist generally exhibit metal–organic barriers and injection characteristics that are not symmetric. Single atoms diffused in the organic film at the metal-on-organic interface play the role of dopants and induce very different electronic states than the metal surface at the organic-on-metal interface. As an example, we recently performed a comparative study of Au-on-F_{16}CuPc (hexadecafluoro copper phthalocyanine) versus F_{16}CuPc-on-Au, and found the HOMO position to be at least 0.5 eV higher (with respect to the metal Fermi level) at the former interface [19].

As a final note, the Alq_3 valence states shift by 0.6 eV toward higher binding energy with the deposition of 2 Å of Mg (Fig. 5), corresponding to a downward level bending. The Alq_3 is originally deposited on an Au substrate, and the E_{FO} position at the surface of the 100 Å pristine film is 2.2 eV above the HOMO, as defined by the 1.8 eV hole barrier at the Au/Alq_3 back interface plus some thickness-dependent shift (presumably due to photoemission-induced charging). The amount of level bending measured upon Mg (or Al) deposition will therefore depend on the initial Fermi level position at the back interface as well as on the final Fermi level position determined by the gap states. The 2 Å Mg do not form a continuous metallic layer, but diffuse and react with Alq_3. The level bending is the direct result of surface and subsurface Fermi level pinning by the chemistry-induced gap states. The extent of the Mg penetration is not precisely known, so the depth of the depletion region is still unclear. However, the small thickness of the organic film (~100 Å) used in the photoemission experiment makes it likely that the film is completely depleted and that the level bending extends all the way to the back interface.



(a) (b)

Fig. 5. (a) UPS spectra as a function of Mg deposition on Alq_3 and (b) illustration of Mg-induced level bending.

4. Summary

The interface gap states observed at the Mg- and Al-Alq_3 interfaces correspond to the organo-metallic complex formed by exothermic chemical reaction and charge transfer between metal atoms and organic molecules. We have shown that these states pin the Fermi level close to the Alq_3 LUMO at the interface regardless of the deposition sequence and, in the process, define the interface dipole and the carrier injection barriers measured at these interfaces. The link between the chemistry-induced interface states and the injection barriers provide a logical explanation for the identical injection current characteristics observed at the metal-on-top and organic-on-top contacts.

Acknowledgements

Support of this work by the MRSEC program of the National Science Foundation (DMR-9809483) and by the New Jersey Center for Optoelectronics is gratefully acknowledged. The authors thank J. Schwartz for useful discussions.

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