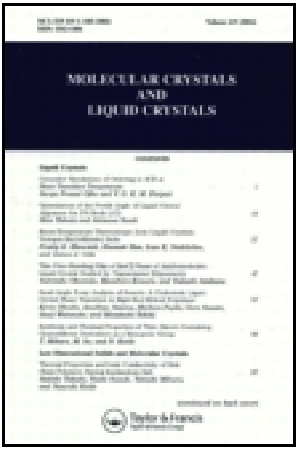

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Electronic Properties of Metal-Organic Interfaces with Application to Electroluminescent Devices

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Electronic Properties of Metal-Organic Interfaces with Application to Electroluminescent Devices

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The electronic structure of metal-organic molecular semiconductor interfaces is investigated via photoemission spectroscopy. We measured the energy offsets between the organic molecular levels and the metal Fermi level, which correspond to the charge injection barriers. Chemical reaction and interdiffusion dominate the behavior of metal-on-top contacts. Organic-on-top interfaces are found to be more abrupt. The present data demonstrate that the rule of vacuum level alignment breaks down and that the effect of electronic gap states cannot be neglected at these interfaces.

Keywords: organic molecular solids; interfaces; metal contacts; heterojunctions

INTRODUCTION

Organic molecular solids have attracted a great deal of attention over the past few years in view of promising applications in electroluminescent devices[1] and thin film transistors[2]. The structural flexibility of molecular thin films opens the door to complex multimaterial structures which lead to a large variety of devices. This flexibility is due to the molecular nature of the materials. Molecular films do not require lattice-matched epitaxial growth to produce device-quality structures, and this property has been extensively exploited in organic light emitting diodes (OLED) and, more recently, optically pumped lasers[3].

OLEDs made of vacuum-deposited molecular films typically comprise two or three layers of different organic materials sandwiched between metal electrodes. In a two-layer heterojunction OLED, holes are injected from a high work function anode into a hole-transport (HT) layer and electrons are injected from a low work function cathode into an electron-transport (ET) layer. The latter is generally also the emissive layer. The electron-hole capture, exciton formation and radiative recombination occur in the emissive layer near the organic heterojunction. The electronic structure of the metal/organic and organic/organic interfaces are therefore central to the performance of the device. In particular, understanding the mechanisms which control the alignment of interface molecular levels and the resulting charge injection barriers is of great importance and can go a long way toward allowing a more directed engineering of devices. In that respect, photoemission spectroscopy (PES) is a very useful tool which, in conjunction with the deposition of organic thin films in ultra-high vacuum, allows direct probing of the electronic structure and chemistry of organic interfaces. We present in this paper the results of such studies on a number of metal/organic interfaces. The results and those from other groups are beginning to provide a coherent picture of molecular organic interfaces.

EXPERIMENTAL CONSIDERATIONS

All experiments were performed in ultra-high vacuum (base pressure = $1\text{x}10^{-10}$ Torr). Organic thin films were grown by sublimation from sources of purified materials at rates of 5-20Å/minute. The base substrates were Si wafers covered with a thick layer of Au. Interfaces were built incrementally in order to follow the development of the interface electronic structure. All depositions were performed at room temperature.

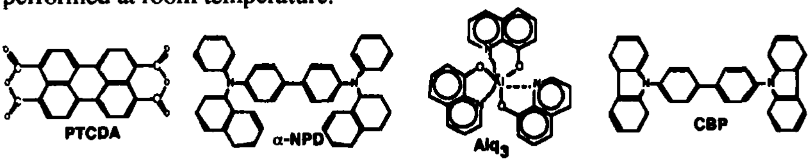

FIGURE 1 Chemical structure of molecules used in this work.

The organic materials used in this work were the HT materials α-NPD (N,N'-diphenyl-N,N'-bis(l-naphthyl)-l,l'biphenyl-4,4''diamine; and PTCDA (3,4,9,10 perylenetetracarboxylic dianhydride); the EL emissive Alq$_3$ (tris(8-

hydroxy-quinoline)aluminum); and CBP (4,4'-N,N'-dicarbazolyl-biphenyl). Chemical structures are given in Fig. 1 The thickness of the organic film was kept in general below 100Å to prevent charging during PES. The metals investigated had work functions ranging between 3.7 eV for Mg and 5.2 eV for Au. All metals were deposited by thermal evaporation.

The energy of the molecular levels was measured via ultra-violet photoemission (UPS) using a He discharge lamp. (hv=21.22 eV for HeI or 40.8 eV for HeII). The resolution of the measurement was 0.15 eV. At each stage of interface formation, the valence states and onset of photoemission were recorded. The position of the highest occupied molecular orbital (HOMO), E_{HOMO}, was determined. The onset of photoemission (E_{ONSET}), which represents the vacuum level (E_{vac}) of the system, was measured with a -3 V bias on the sample to clear the vacuum level of the detector. The ionization energy (IE) of each organic, determined following the standard formula: $EI = hv - [E_{HOMO} - E_{ONSET}]$, is given in Table 1.

TABLE 1: Optical band gap, ionization energy (IE) and electron affinity (EA) of the molecular films used in this work

	Optical gap (eV)	IE (eV)	EA (eV)
PTCDA	2.2	6.8	4.6
Alq_3	2.7	5.8-6.0	3.1-3.3
α-NPD	3.1	5.4-5.6	2.3-2.5
CBP	3.1	6.1-6.3	3.0-3.2

RESULTS AND DISCUSSION

We distinguish between metal-on-top and organic-on-top configurations. Interfaces of the former type are generally more complex than the latter in view of the damage that the hot metal atoms can cause when adsorbing on the soft organic surface. Metal-on-top interfaces generally undergo more extensive metal-organic reactions and interdiffusion of the adatoms into the organic bulk. This is not necessarily detrimental to carrier injection, however, and recent work on metal-organic pairs has actually shown superior performance of the metal-on-top configuration[4]. We describe here one of these examples before looking at the more easily characterized organic-on-top interfaces.

Metal-on-top vs. Organic-on-top Configurations

Mg (alloyed with Ag) has been shown to form an efficient electron injecting contact to Alq_3 and is extensively used in OLEDs[1]. The low work function of Mg (3.7 eV) lowers the barrier for electron injection between the metal Fermi level (E_F) and the Alq_3 lowest unoccupied molecular orbital (LUMO). Recent UPS measurements[5] indeed show that the interface position of E_F(Mg) is 0.1 eV below the Alq_3 LUMO for the Mg-on-top configuration and 0.2 eV below for the Alq_3-on-top configuration (Note: the LUMO position is simply deduced from the measured HOMO position by adding the optical gap). In spite of very similar barriers, however, the Mg-on-top contact leads to OLEDs with higher efficiency[4], presumably due to easier electron injection. It is therefore important to understand the differences between the morphology and/or electronic structure of these two interfaces.

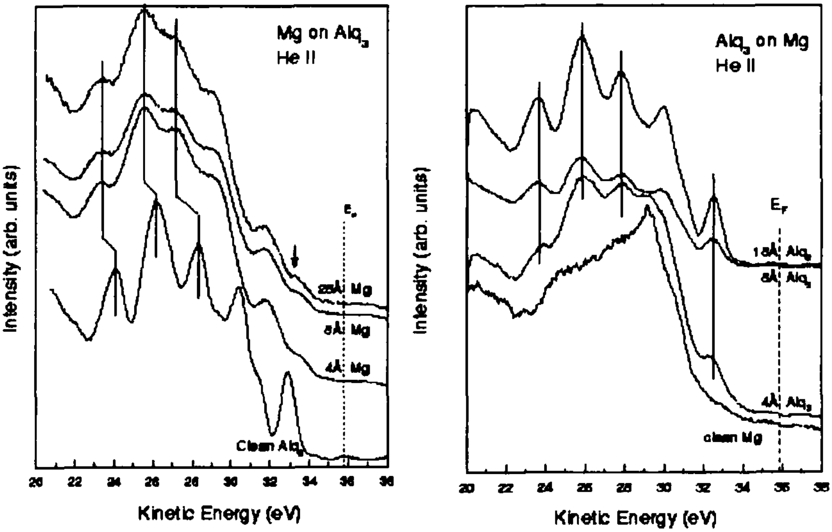

FIGURE 2 (left) UPS spectra for Mg deposited on Alq_3. Broken vertical lines underline the Mg-induced shift and the arrow indicates the position of Mg-induced states. (right) UPS spectra for Alq_3 deposited on Mg.

The UPS spectra for Mg-on-top and Alq_3-on-top underline several significant differences between the two interfaces (Fig. 2). The first concerns the interface morphology. In the case of Alq_3-on-top, the organic layer rapidly buries the Mg substrate, indicative of an abrupt interface. The line-shape of the pure Alq_3 valence spectrum is obtained with the deposition of only a few molecular layers, whereas in the case of Mg-on-top, there is no evidence of surface accumulation of Mg, such as a Fermi edge or a drastic change in valence state line shape, even with 28Å Mg. Auger and X-ray photoemission spectroscopy measurements confirm the presence of Mg, thus indicating that the metal atoms diffuse into the organic layer. The second difference pertains to interface states. Mg deposited on Alq_3 induces a shift of the valence spectrum toward higher binding energy and brings the HOMO position to nearly the same position with respect to E_F than that obtained for Alq_3 deposited on Mg (see above). In addition, however, new electronic states appear in the Alq_3 gap above the HOMO, whereas no similar states are seen in Fig. 2b. These states are attributed to a chemical reaction (Birch-type reaction[5]) between Mg ions diffusing in the organic film and the Alq_3 molecules. The reaction in the Alq_3-on-top case, if it exists, is limited to the interface. It is believed that the superior quality of Mg-on-top contact over the abrupt Alq_3-on-top contact is linked to the presence of these gap states which help the electron (hole) to hop up (down) from E_F to the LUMO (HOMO) in the interdiffused and reacted region.

A similar behavior, leading to the formation of a large density of interface states, was noted for other reactive interfaces like In, Ti or Sn on PTCDA[6]. Although these metals lead to HOMO and LUMO positions identical to those induced by Au and Ag with respect to E_F, they form good injection contacts whereas the noble metals do not. Another example is copper phthalocyanine (CuPc)-indium-tin-oxide (ITO)[7]. Although the ITO Fermi level appears to be close to the HOMO of CuPc (ϕ(ITO)=4.5 eV vs. IE(CuPc)=4.8 eV), thus making ITO a good hole injector, ITO *deposited* on CuPc also appears to form a good electron injector, presumably because of the damage it causes and the gap states it introduces in the gap of the organic materials.

Electronic Structure of Organic-on-top Interfaces

Interfaces formed by depositing organic films on metals are considerably more abrupt and lend themselves to easier interpretations of their electronic structure. The issue investigated here is the dependence of the hole and electron injection barriers on the metal work function. It was generally expected that organic-metal interfaces would follow the vacuum level alignment rule, according to which the electron (hole) barrier should be defined by the difference between the metal work function and EA (IE) of the organic solid (Fig. 3a). Accordingly, the barriers should vary as $S\times$(metal work function) where the proportionality factor S equals unity.

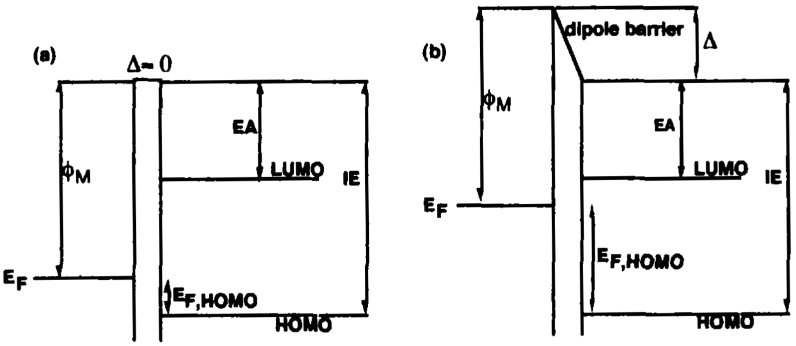

FIGURE 3 Schematic of an organic/metal interface (a) without and (b) with a positive interface dipole barrier Δ. Note the difference in $E_{F,HOMO}$

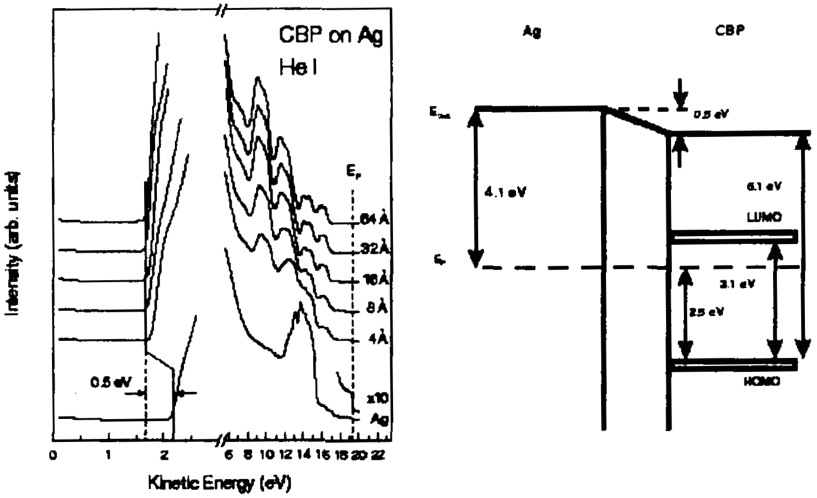

FIGURE 4 (a) UPS spectra as a function of CBP deposition on Ag. The vacuum level shift is deduced from the shift in photoemission onset. (b) interface energy diagram

However, recent studies have demonstrated that the situation is material-specific, ranging from strong dependence with a slope $S\approx1$ for organics like ZnTPP[8] to nearly independent of the metal with a slope $S\approx0$ for PTCDA[9]. It was also shown that interfaces generally exhibit a vacuum level shift, or dipole barrier Δ, between the two solids[10]. This dipole makes up the difference between the interface E_F position expected from the vacuum level alignment rule and the actual position (Fig. 3b). As an example, Fig. 4a shows the UPS spectra for the formation of the CBP/Ag interface[12]. The valence spectrum of the metal shows the Fermi edge and the Ag 4d level. A deposition of 16Å CBP produces a spectrum very close to that of a thick CBP film. The E_F-HOMO energy difference is given in Fig. 4b. Concomitant with the change to the CBP spectrum is a 0.5 eV shift in photoemission onset toward lower kinetic energy, indicating a decrease in vacuum level across the interface and the formation of a dipole barrier (Fig. 4b).

A summary of our interface data is given in Fig. 5. The HOMOs of the four organics are arbitrarily aligned at E=0. Each data point corresponds to the measured position of E_F with respect to the HOMO, i.e. $E_{F,HOMO}$, at a specific organic-metal interface The dashed line gives the position of E_F vs. metal work function corresponding to vacuum level alignment between the two solids. The difference between the dashed line and the data points is the interface dipole barrier (vertical lines).

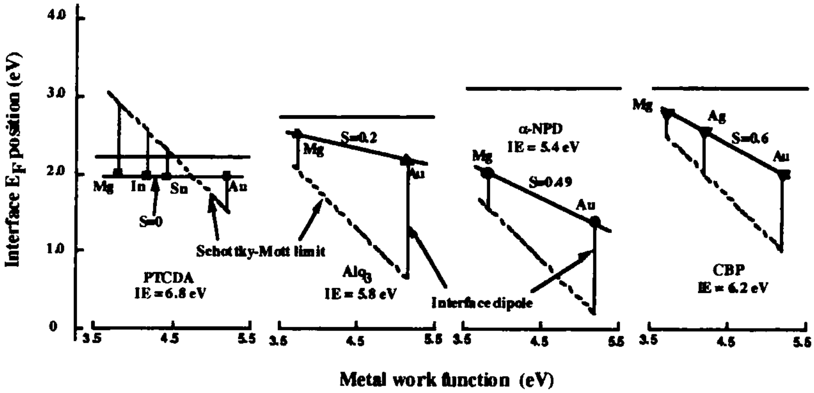

FIGURE 5 $E_{F,HOMO}$ for PTCDA, Alq$_3$, α-NPD and CBP as a function of metal work function. The dashed lines correspond to $S=1$ and the vertical lines show the magnitude of the interface dipole.

In most cases, the dipole barrier is positive (i.e., as defined in Fig. 3), but can also be negative for metal work functions close to or smaller than the organic EA. (e.g. for Mg, In and Sn on PTCDA). It can also be large, reaching more than 1 eV for Au on Alq$_3$ and α-NPD. Neglecting the dipole can therefore lead to significant errors in the description of the interface electronic structure.

The presence of the dipoles indicates that the movements of the Fermi level with metal work function are somewhat restricted, and more so in PTCDA and Alq_3 than in α-NPD and CBP (Fig. 5). It is interesting to note that surface "pinning" of E_F on inorganic semiconductors is also more severe for low band gap materials, e.g. Si or GaAs, than for high band gap materials, e.g. ZnSe or GaN. Models based on varying densities of interface states justify these differences. It is likely that interface gap states due to defects or intrinsic boundary condition effects do play a similar role for organic molecular solids. Their origin, however, is yet to be determined.

SUMMARY

We have presented results of photoemission studies which demonstrate a break down of the vacuum alignment rule at all metal-organic interfaces investigated. Large dipole barriers, which cannot be ignored in the modeling of the interface electronic properties, are found at most of these interface. The restricted movement of the Fermi level, which leads to these dipoles, is due to interface states, the origin of which is yet to be uncovered.

Acknowledgements

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