Molecular level alignment at organic semiconductor-metal interfaces

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In order to clarify the electronic structure of metal-molecular semiconductor contacts, we use photoemission spectroscopy to investigate the energetics of interfaces formed by vacuum deposition of four different molecular thin films on various metals. We find that the interface electron and hole barriers are not simply defined by the difference between the work functions of the metals and organic solids. The range of interface Fermi level positions is material dependent and dipole barriers are present at all these interfaces. The results demonstrate the breakdown of the vacuum level alignment rule at interfaces between these organic molecular solids and metals. © 1998 American Institute of Physics. [S0003-6951(98)02831-9]

The injection of carriers at metal contacts to organic semiconductors is central to the operation of organic-based devices. High device efficiency, low turn-on voltages, and long lifetimes require low resistivity and chemically stable contacts. Technology has so far relied on empirical solutions to these problems and there is considerable incentive at this point to further our understanding of the electronic structure and chemical properties of metalorganic interfaces.1–12

The subject of this letter is one which has long been debated for metal/inorganic semiconductor junctions, namely, the degree to which the barriers vary with the metal work function (φM). At metal/organic semiconductor interfaces, the hole and electron barriers (φBe and φBh in Fig. 1) depend on the position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with respect to the metal Fermi level (EF). If the vacuum level alignment rule were to hold at these interfaces, φBh would be the difference between the ionization energy (IE) of the organic film and φM [Fig. 1(a)]. Conversely, φBe would be by the difference between φM and the electron affinity (EA) of the organic film. One generally defines an interface parameter SB which gives the variation of the barrier as a function of φM, i.e., φBe=SB×φM. The vacuum alignment rule corresponds to |SB|=1. Known as the Schottky–Mott limit for inorganic semiconductor interfaces, the vacuum level alignment rule had been expected to hold for the weakly interacting interfaces formed by organic solids. So far, the results on this point have been mixed and have revealed material specific behaviors. Transport and electroabsorption measurements for metal-MEH-PPV interfaces7,8 and photoemission spectroscopy (PES) studies of porphyrins5 or ZnTPP10 on metals have shown nearly Schottky–Mott-like behavior. On the other hand, interfaces with Alq3,5,12 DP-NTCl,3 H2TPP,5 or PTCDA4 deviate from the vacuum level alignment rule. In the latter three cases we have shown the interface Sb parameters well below unity. Dipole barriers which compensate for the difference between the work functions of two solids have been found to approach 1 eV at some of these interfaces. Ignoring these barriers, as is generally done in the literature, may therefore lead to significant errors in the prediction of the electronic properties of these interfaces.

We present here the result of an extensive investigation involving several metals and organic semiconductors. The four molecular solids are the electron-transport emissive material tris(8-hydroxy-quinoline)aluminum (Alq3), the two hole-transport materials 3,4,9,10 perylenetetracarboxylic dihydride (PTCDA) and (N,N’-diphenyl-N,N’-bis(1-naphthyl)-1,1’-biphenyl-4,4”-diamine (α-NPD), and 4,4’-N,N’-dicarbazolyl-biphenyl (CBP). The interfaces are formed by vacuum evaporation of the organic films on top of the metal substrates. Because of the much lower heat of adsorption of the molecules and the higher stability of the metal surfaces, these interfaces are more abrupt than those obtained by reverse deposition sequence4,12 and thus lend themselves to an easier interpretation of their electronic structure. The results show a material-specific behavior, with barely nearly independent of the metal for PTCDA and substantially dependent for Alq3, CBP, and α-NPD. At all of

FIG. 1. Schematic of an organic-metal interface energy diagram (a) without and (b) with an interface dipole Δ. φBe and φBh are the electron and hole barriers, and E_{val}(O) and E_{val}(M) are the organic and metal vacuum levels, respectively.

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these interfaces, the measurements demonstrate the presence of interface dipole barriers and the breakdown of the vacuum level alignment rule.

All experiments were performed in an ultrahigh vacuum system (10\(^{-10}\) Torr) composed of a preparation chamber for organic deposition and an analysis chamber. The metals investigated were Mg, In, Ag, Sn, and Au. Fresh films of Au were evaporated on silicon wafers with an intermediate layer of chromium to improve wetting. Mg and Ag films were evaporated on top of the Au films. Fresh In and Sn surfaces were obtained by evaporation of thick In and Sn layers on sputter-cleaned foils of the same metal. The organic-metal interfaces were formed by incremental molecular beam evaporation. Details on the evaporation conditions for the organic layers have been given elsewhere.\(^{4,13-15}\) Synchrotron radiation photoelectron spectroscopy (PES) (photon energy \(h\nu=82\) eV) was used for PTCDA on In and Sn, Alq\(_3\) on Au, and \(\alpha\)-NPD on Au. PTCDA on Mg and Au, Alq\(_3\) on Mg and Ag, \(\alpha\)-NPD on Mg and CBP on Mg, Ag, and Au were investigated with ultraviolet PES performed with a He discharge lamp (\(h\nu=21.22\) or 40.8 eV). In both cases, the electron analyzer was a double-pass cylindrical mirror analyzer and the overall resolution of the measurement was 150 meV. \(E_F\) was measured systematically on each metallic substrate.

The work function of each metal substrate was obtained by measuring the top of the occupied band, \(E_F\) in this case, and the vacuum level (\(E_{\text{vac}}\)) given by the onset of photoemission (\(E_{\text{onset}}\)), i.e., \(\phi_M=-h\nu-(E_F-E_{\text{onset}})\). The valence states of the organic films, the position of the top of the HOMO with respect to \(E_F\) (\(E_{\text{HOMO}}=E_F-E_{\text{HOMO}}\)) and \(E_{\text{onset}}\) were recorded for each film thickness. The top of the valence states, \(E_{\text{HOMO}}\), was determined by linear extrapolation of the high kinetic energy side of the HOMO peak. The \(E_{\text{vac}}\) and \(E_{\text{HOMO}}\) used for interpreting the interface electronic structure were measured on 5–10 Å films, a thickness typically sufficient to provide well-resolved molecular features while preventing uncertainties due to electrostatic effects such as “band bending” or charging. The ionization energies of the organic films, defined as \(IE=h\nu-(E_{\text{HOMO}}-E_{\text{onset}})\), are 6.8 eV for PTCDA, 5.8 eV for Alq\(_3\), 5.4 eV for \(\alpha\)-NPD, and 6.3 eV for CBP. These numbers typically fluctuate by \(\pm 0.2\) eV due to variations in surface morphologies and molecular orientation.

The schematic of an organic-metal energy diagram with and without interface dipole is given in Fig. 1. Part (a) illustrates the Schottky–Mott limit corresponding to the alignment of vacuum levels across the interface (\(\Delta=0\)) and giving \(E_{\text{HOMO}}=IE-\phi_M\). In the finite dipole case [part (b)], the position of \(E_F\) in the gap of the organic solid is determined in part by intrinsic states or by states induced by the metal (defects or other). The difference between the work functions of the two solids is accounted for by the interface dipole barrier \(\Delta\). The barrier represented in Fig. 1(b), which we define as positive, corresponds to a positive (negative) charge on the organic (metal) side of the interface.

The experimental values of \(E_{\text{HOMO}}\) are plotted in Fig. 2 for each organic material as a function of metal work function. The HOMO levels are arbitrarily aligned at \(E=0\) and the LUMO levels are positioned according to the optical gap of each material (neglecting exciton binding energy and relaxation effects). The oblique dashed lines represent the zero-dipole (\(|S|_{\beta}=1\)) limit. The data show a significant departure from that limit. \(E_F\) is essentially “pinned” near the top of the gap for PTCDA (\(|S|_{\beta}=0\)). The energy span is larger with \(\alpha\)-NPD (\(|S|_{\beta}=0.49\)), CBP (\(|S|_{\beta}=0.6\)), and Alq\(_3\) (\(|S|_{\beta}=0.9\)). Dipoles are found at all interfaces.

At the molecular level, the mechanisms which restrict barrier variations are unknown at this time. Gap states induced by the deposition of metals on organic surfaces have been seen, in particular for In, Sn, Al, and Ti on PTCDA\(^4\) and Mg on Alq\(_3\).\(^{12}\) In these cases, the diffusion of a large number of metal atoms into the organic and the reaction with molecules give rise to large densities of gap states easily detectable via PES. In the present case, the abruptness of the interface limits the extent of the interaction and makes similar states more difficult to detect. A similar situation exists at inorganic semiconductor interfaces. The effect is nevertheless likely to be related to extrinsic or intrinsic gap states which exist at the surface of the film or are induced by the formation of the interface.

From Fig. 1, the difference between the measured \(E_{\text{HOMO}}\) and the theoretical value corresponding to the \(\Delta=0\) limit (dashed line) should be the interface dipole barrier. The experimental values of this barrier, obtained from the shift of the photoemission onset for each organic-metal pair, are plotted in Fig. 3 as a function of \(\phi_M\). The interfaces between Mg, In, and Sn and PTCDA which has large IE and
The slopes given in Figs. 2 and 3 lead to 1.0 and 1.02 for PTCDA and a organic material are therefore difficult to explain. Faces, and the reasons for the present restriction to one bond and the large pool of metal charges anchor the energy interfaces with metals, however, the organic-metal substrate energy levels of these quasi-insulating molecular solids. At charges injected in the material is likely to affect the bulk equilibrium conditions. Under bias, the large density of energy barriers. In all but one case, the magnitude and sign of the dipole barrier matches the difference between the metal work function and the “work function” of the organic solid. Discrepancies in this relationship may be caused by variations in measured IEs due to variations in organic film morphology. Finally, the data suggest that chemistry must be taken into account to explain transport properties at these interfaces.

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