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 (ϕ_M). At metal/organic semiconductor interfaces, the hole and electron barriers (ϕ_{Bh} and ϕ_{Be} 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 (E_F). If the vacuum level alignment rule were to hold at these interfaces, ϕ_{Bh} would be the difference between the ionization energy (IE) of the organic film and ϕ_M [Fig. 1(a)]. Conversely, ϕ_{Be} would be by the difference between ϕ_M and the electron affinity (EA) of the organic film. One generally defines an interface parameter S_B which gives the variation of the barrier as a function of ϕ_M, i.e., $\phi_B \alpha S_B \times \phi_M$. The vacuum alignment rule corresponds to $|S_B| = 1$. 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 interfaces[7,9] and photoemission spectroscopy (PES) studies of porphyrins[8] or ZnTPP[10] on metals have shown nearly Schottky–Mott-like behavior. On the other hand, interfaces with Alq$_3$,[5,12] DP-NTCI,[5] H$_2$TPP,[5] or PTCDA[4] deviate from the vacuum level alignment rule. In addition, the latter three have been shown to exhibit S_B parameters well below unity. Dipole barriers which compensate for the difference between the work functions of the 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 (Alq$_3$), the two hole-transport materials 3,4,9,10 perylenetetracarboxylic dianhydride (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 sequence[4,12] and thus lend themselves to an easier interpretation of their electronic structure. The results show a material-specific behavior, with barriers nearly independent of the metal for PTCDA and substantially dependent for Alq$_3$, CBP, and α-NPD. At all of
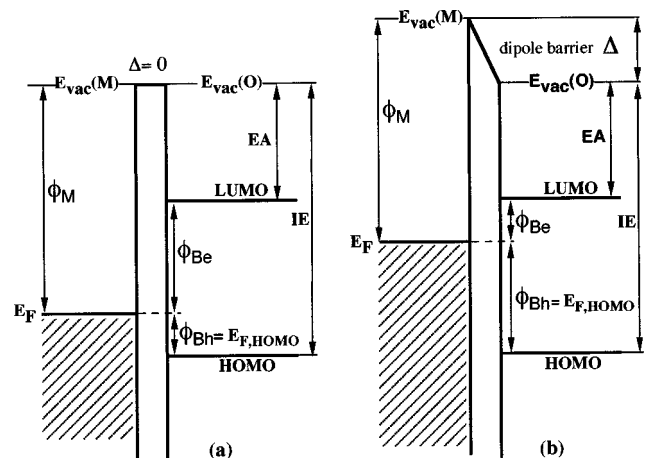

FIG. 1. Schematic of an organic-metal interface energy diagram (a) without and (b) with an interface dipole Δ. ϕ_{Be} and ϕ_{Bh} are the electron and hole barriers, and $E_{vac}(O)$ and $E_{vac}(M)$ are the organic and metal vacuum levels, respectively.

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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 α-NPD on Au. PTCDA on Mg and Au, Alq$_3$ on Mg and Ag, α-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_{vac}) given by the onset of photoemission (E_{onset}), i.e., $\phi_M = h\nu - (E_F - E_{onset})$. The valence states of the organic films, the position of the top of the HOMO with respect to E_F ($E_{F,HOMO} = E_F - E_{HOMO}$) and E_{onset} were recorded for each film thickness. The top of the valence states, E_{HOMO}, was determined by linear extrapolation of the high kinetic energy side of the HOMO peak. The E_{vac} and $E_{F,HOMO}$ 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 $IE = h\nu - (E_{HOMO} - E_{onset})$, are 6.8 eV for PTCDA, 5.8 eV for Alq$_3$, 5.4 eV for α-NPD, and 6.3 eV for CBP. These numbers typically fluctuate by ± 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 $E_{F,HOMO} = IE - \phi_M$. 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 Δ. 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 $E_{F,HOMO}$ 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 re-
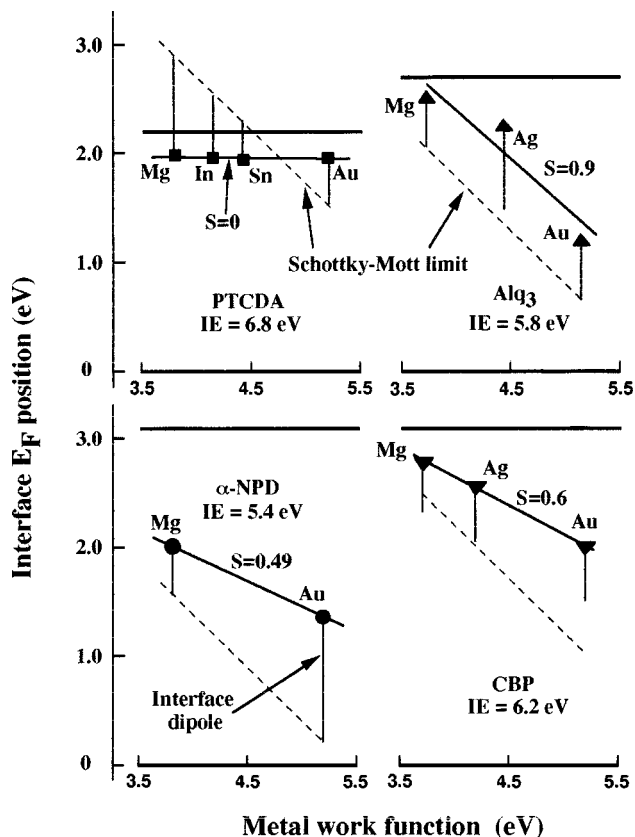

FIG. 2. $E_{F,HOMO}$ for PTCDA, Alq$_3$, and α-NPD as a function of metal work function. The HOMO of the three organics are aligned and each LUMO is positioned according to the optical band gap. The S values are indicated for PTCDA and Alq$_3$. The oblique dashed lines correspond to the Schottky–Mott (zero dipole, $S = 1$) limit and the vertical full lines show the magnitude of the interface dipole barrier Δ.

laxation effects). The oblique dashed line represents the zero-dipole ($|S_B| = 1$) limit. The data show a significant departure from that limit. E_F is essentially ''pinned'' near the top of the gap for PTCDA ($S_B \approx 0$). The energy span is larger with α-NPD ($|S_B| = 0.49$), CBP ($|S_B| = 0.6$), and Alq$_3$ ($|S_B| \approx 0.9$). 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 $E_{F,HOMO}$ 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 ϕ_M. The interfaces between Mg, In, and Sn and PTCDA which has large IE and
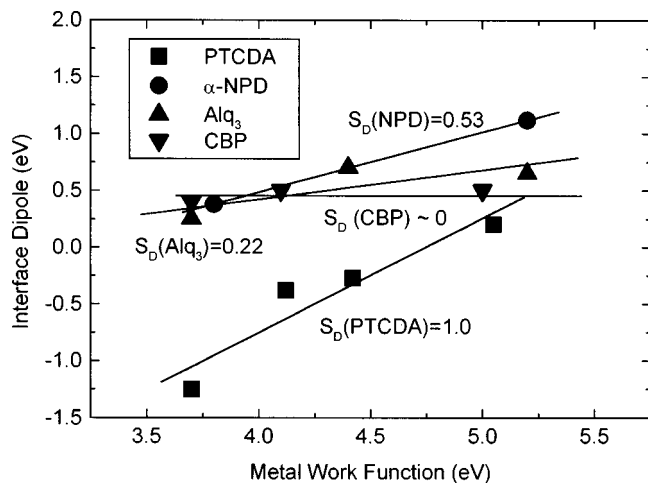
FIG. 3. Plot of the measured interface dipole barrier as a function of metal work function for each organic solid.

EA, exhibit negative charge transfers from the metal to the organic. All other charge transfers are in the opposite direction. Some of the dipole barriers are large, i.e., 1.15 for α-NPD/Au or -1.25 eV for PTCDA/Mg, and neglecting them leads to substantial errors in the description of the interface electronic structure.

We define S_D as the slope of the dipole barrier vs ϕ_M. Assuming that IE is invariant for a given organic material, the situation depicted in Fig. 1(b) implies that the variation of Δ with metal work function is complementary to the variation of $\phi_{Bh} = E_{F,HOMO}$. Consequently, $|S_D| + |S_B| = 1$. The slopes given in Figs. 2 and 3 lead to $|S_D| + |S_B|$ equal to 1.0 and 1.02 for PTCDA and α-NPD, respectively, in excellent agreement with the prediction within experimental error. The difference between the data and the prediction from the $\Delta = 0$ model is therefore entirely compensated by the dipole barrier for these two materials. For Alq$_3$, the sum of the slopes is 1.1. Although the nearly Schottky–Mott behavior of the electron and hole barriers ($|S_B| \approx 0.9$) should result in small interface dipoles, substantial dipoles are observed. The only clear exception to the sum rule is CBP, for which the ionization energy varies by as much as 300 meV with the metal substrate.[15] Morphological variations in the films deposited on various metal surfaces may affect IE. Interestingly, the corresponding interface dipole appears to be independent of the metal work function (Figs. 2 and 3). A similar behavior had been previously reported for ZnTPP[5] and was tentatively attributed to an electrostatic interaction (i.e., image force) at the interface. However, this type of phenomenon would be expected to apply to a broad class of interfaces, and the reasons for the present restriction to one organic material are therefore difficult to explain.

The relation between the PES results and injection characteristics is an important issue. The interface energy picture presented above is obtained from data collected under quasi-equilibrium conditions. Under bias, the large density of charges injected in the material is likely to affect the bulk energy levels of these quasi-insulating molecular solids. At interfaces with metals, however, the organic-metal substrate bonds and the large pool of metal charges anchor the energy structure of the interface, and the energy diagram determined with PES is unlikely to be significantly modified under in-

jection. However, it is remarkable that qualitatively different contacts are obtained with metals which, from a spectroscopic point of view, produce nearly identical barriers. For example, in spite of uniformly large hole barriers (Fig. 2), In and Sn make good hole-injection contacts to PTCDA whereas Au does not. These differences must be linked to the extensive chemical reactions which take place at In(Sn)/PTCDA[4] interfaces. The metals diffuse into the film and react with the molecules, creating in the process a large density of states which leads to carrier tunneling and hopping across the interface.

In summary, we have shown that the molecular organic semiconductors PTCDA, Alq$_3$, α-NPD, and CBP deposited on metals form interfaces which do not follow the expected vacuum level alignment rule. Dipole barriers are found at all interfaces. The variations of the electron and hole barriers with metal are material dependent. Interface chemical bonds presumably play an important role in the control of these 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.

[1] W. R. Salaneck and J. L. Brédas, Adv. Mater. **8**, 48 (1996).
[2] S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, and K. Yamashita, Appl. Phys. Lett. **67**, 1899 (1995).
[3] Y. Park, V. Choong, E. Ettedgui, Y. Gao, B. R. Hsieh, T. Wehrmeister, and K. Müllen, Appl. Phys. Lett. **69**, 1080 (1996).
[4] Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, and S. R. Forrest, Phys. Rev. B **54**, 13748 (1996).
[5] H. Ishii and K. Seki, IEEE Trans. Electron Devices **44**, 1295 (1997).
[6] S. T. Lee, X. Y. Hou, M. G. Mason, and C. W. Tang, Appl. Phys. Lett. **72**, 1593 (1998).
[7] I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).
[8] Y. Harima, H. Okazaki, Y. Kunugi, K. Yamashita, H. Ishii, and K. Seki, Appl. Phys. Lett. **69**, 1059 (1996).
[9] I. H. Campbell, J. P. Ferraris, T. W. Hagler, M. D. Joswick, I. D. Parker, and D. L. Smith, Polym. Adv. Technol. **8**, 417 (1997).
[10] D. Yoshimura, H. Ishii, S. Narioka, M. Sei, T. Mayazaki, Y. Ouchi, S. Hasegawa, Y. Harima, K. Yamashita, and K. Seki, J. Electron Spectrosc. Relat. Phenom. **78**, 359 (1996).
[11] K. Sugiyama, D. Yoshimura, E. Ito, T. Miyazaki, Y. Hamatani, I. Kawamoto, H. Ishii, Y. Ouchi, and K. Seki, Synth. Met. **86**, 2425 (1997).
[12] A. Rajagopal and A. Kahn, J. Appl. Phys. **84**, 355 (1998).
[13] A. Rajagopal and A. Kahn, Adv. Mater. **10**, 140 (1998).
[14] A. Rajagopal, C. Wu, and A. Kahn, J. Appl. Phys. **83**, 2649 (1998).
[15] I. Hill and A. Kahn, J. Appl. Phys. (to be published).