Band alignment at organic-inorganic semiconductor interfaces: α-NPD and CuPc on InP(110)

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We present a photoemission study of the electronic properties of organic-inorganic semiconductor heterojunctions formed between the two hole transport materials, N,N′-diphenyl-N, N′-bis(1-naphthyl)-1-1′biphenyl-4,4″diamine (α-NPD) and copper-phthalocyanine (CuPc), and InP(110). The highest occupied molecular orbital of α-NPD (CuPc) is found to be 0.2 eV below (0.2 eV above) the InP valence band maximum, leading to a staggered (nested) energy level configuration. The α-NPD/InP and CuPc/InP interfaces exhibit 0.4 and 0.65 eV interface dipole barriers, respectively, that indicate a displacement of negative charge from the organic film to the inorganic substrate. This charge displacement is found to be consistent with the relative ionization energies and electron affinities of the materials. © *1999 American Institute of Physics.*
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I. INTRODUCTION

Thin films of organic molecular semiconductors have been the focus of numerous investigations over the past few years in view of promising applications in opto- and microelectronics.[1,2] The endless potential for organic materials synthesis and the structural flexibility of molecular thin films due to the closed shell nature of molecules and the weak intermolecular bonding leads to a variety of possible structures and combinations unmatched by any other class of materials. These properties are being exploited particularly successfully in the fabrication of vacuum deposited organic multilayers for light emitting devices.[2]

The chemistry and electronic properties of organic interfaces are central to the behavior of thin-film-based devices. Metalorganic interfaces have received considerable attention in view of their dominant role in the injection of carriers into organic thin films.[3–9] Organic-organic heterojunctions have also been extensively investigated for their role in carrier transport in multilayer light emitting structures.[10,11] Organic-inorganic (OI) semiconductor heterojunctions, however, have received only limited attention[12] because they are not central to current devices. They could, however, become relevant to future hybrid OI devices requiring materials with complementary functionality which cannot be made with structurally incompatible inorganic materials. There is therefore fundamental, as well as practical incentive to investigate the electronic structure of heterojunctions formed between a well-known inorganic compound like InP and organic molecular materials. Mechanisms of interface bonding and alignment of molecular levels across these OI heterojunctions are all but unknown, and deserve attention. We report here on photoemission studies of OI interfaces formed by depositing thin films of N,N′-diphenyl-N,N′-bis(1-naphthyl)-1-1′biphenyl-4,4″diamine (α-NPD) and copper-phthalocyanine (CuPc) on InP(110). The chemical structure of these molecules are shown in Fig. 1. In each case, the valence band offset, i.e., the energy difference between the inorganic valence band top and the organic highest occupied molecular orbital (HOMO) is determined. The vacuum level alignment rule is found to break down at both interfaces, confirming the results obtained at most metalorganic interfaces.

II. EXPERIMENT

The photoemission experiments were performed in an ultrahigh vacuum system consisting of an analysis chamber and a preparation chamber. The analysis chamber (base pressure 10^{-10} mbar) was equipped with a He discharge lamp and a double-pass cylindrical mirror analyzer for ultraviolet photoemission spectroscopy (UPS). The preparation chamber (base pressure 5×10^{-10} mbar) was equipped with evaporation sources for the organic molecules and a quartz microbalance. InP(110) surfaces were prepared by cleaving *in situ* prenotched p-type (10^{18} cm^{-3}) bars using a fracture stage. The deposition of the organic films was performed on room temperature InP at rates of 0.1–2 nm/min. The α-NPD and CuPc densities were assumed to be equal to 1.5 g/cm^3. No correction for sticking coefficients different from unity was applied. All electron sources, including vacuum gauges, were switched off during deposition and UPS measurements in order to minimize damage to the organic layers. The resolution of the UPS measurements (~0.2 eV for He II) and the position of the Fermi energy (E_F) were determined from the Fermi edge of freshly deposited thick silver films. The low-energy onset of electron emission, which gives the position

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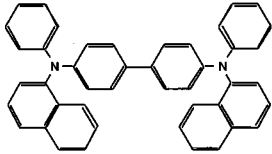
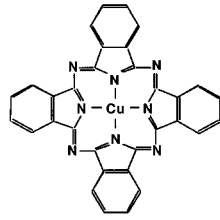• **α-NPD**   • **CuPc**

FIG. 1. Chemical structure of N,N′-diphenyl-N,N′-bis(1-naphthyl)-1-1′biphenyl-4,4″diamine (α-NPD) and copper-phthalocyanine (CuPc).

of the vacuum level (E_{vac}), was measured with a -3 V bias voltage applied to the sample to clear the detector work function.

III. RESULTS

A. NPD

He II UPS spectra recorded for incremental depositions of α-NPD or InP(110) are shown in Fig. 2. The bottom spectrum corresponds to the clean cleaved substrate, and exhibits the features of the InP angle-integrated valence spectrum. The valence features of the organic film dominate the UPS spectrum for the smallest film thickness investigated (0.5 nm), suggesting that the semiconductor substrate is already entirely covered at this stage. The fine structure of the molecular levels evolves with increasing thickness, leading to a clearly resolved HOMO peak at 1.5 nm. The thickest film investigated (4.5 nm) exhibits the pronounced features typical of molecular levels. The spectrum is in excellent agree-
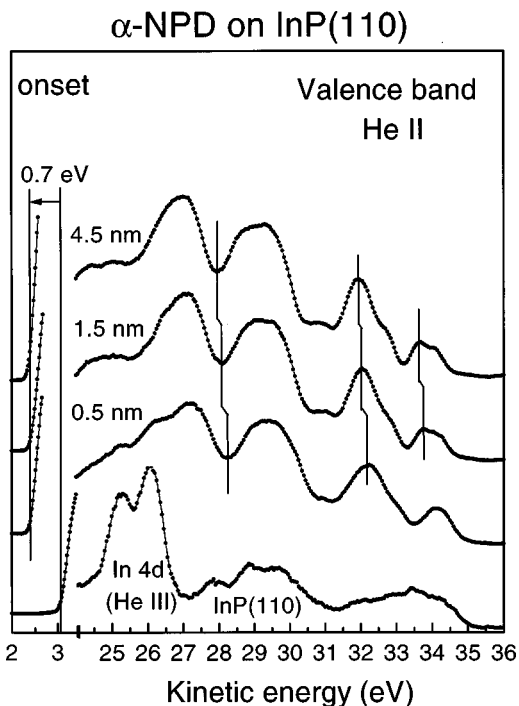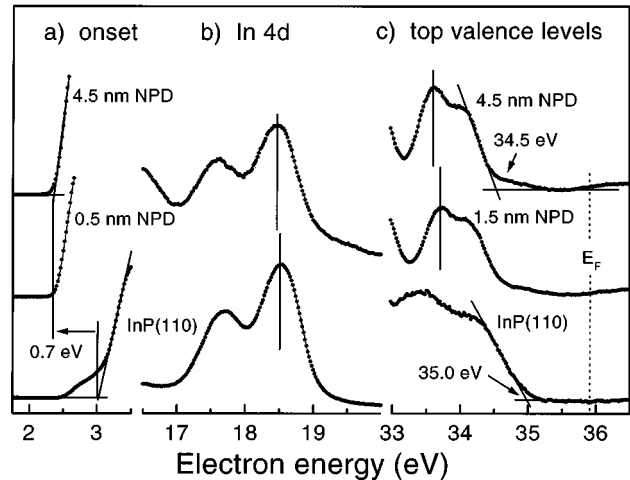

FIG. 3. Photoemission onset, In $4d$ core level, and top of the valence states as a function of α-NPD thickness on InP(110).

ment with data recently obtained for thick α-NPD films deposited on gold.[11] The lower binding energy valence peaks of the α-NPD film are attributed predominantly to the π-orbitals of the molecule, while the higher binding energy peaks have increasing σ-like character.

The ionization energy (IE) of a semiconductor surface is determined via photoemission spectroscopy by adding the photon energy to the onset of photoemission (E_{ONSET}) to obtain the vacuum level (E_{VAC}), and taking the linear extrapolation of the low binding energy edge of the valence spectrum to determine the top of the valence level (E_V for the inorganic semiconductor, E_{HOMO} for the organic semiconductor). Thus, $IE = E_{VAC} - E_V = h\nu - (E_V - E_{ONSET})$. We obtain $IE^{InP} = 5.8 \pm 0.15$ eV, in very good agreement with previously published data.[13] E_V^{InP} is 0.9 eV below E_F on the clean p-type InP surface (Fig. 3), indicating a downward band bending due to cleavage induced defects. $IE^{\alpha\text{-NPD}}$ is obtained from $E_{ONSET}^{\alpha\text{-NPD}}$ and $E_{HOMO}^{\alpha\text{-NPD}}$ of the 4.5 nm film (Figs. 1 and 2) and is equal to 5.6 ± 0.15 eV, also in close agreement with recently published values.[10,11]

The energy offset between the top of the InP valence band and the top of the α-NPD HOMO at the interface is determined using E_V^{InP} of the clean substrate and $E_{HOMO}^{\alpha\text{-NPD}}$ of the 4.5 nm film, and correcting for the band bending induced in the substrate by the deposition of the organic film, and in the organic film away from the interface. The uncorrected energy difference is 0.5 eV (Fig. 3). The overlayer-induced InP band bending is measured from the shift of the In $4d$ core level between the clean substrate and the substrate covered by 0.5 nm α-NPD (Fig. 3). The In $4d$ peak shifts by 50 meV toward higher binding energy, indicating a corresponding increase in downward band bending in the substrate. No indication of further band bending is obtained at higher coverage. On the organic side of the interface, a 0.25 eV shift of the molecular levels toward higher binding energy occurs with increasing organic film thickness (Figs. 2 and 3), indicating some band bending away from the interface. The corrected interface valence level offset is 0.2 ± 0.1 eV, with the

FIG. 2. He II valence band and photoemission onset for increasing thickness of α-NPD on InP(110). Broken vertical lines indicate band bending in the organic film. The In $4d$ peak overlapping the He II valence band is due to the He III radiation.
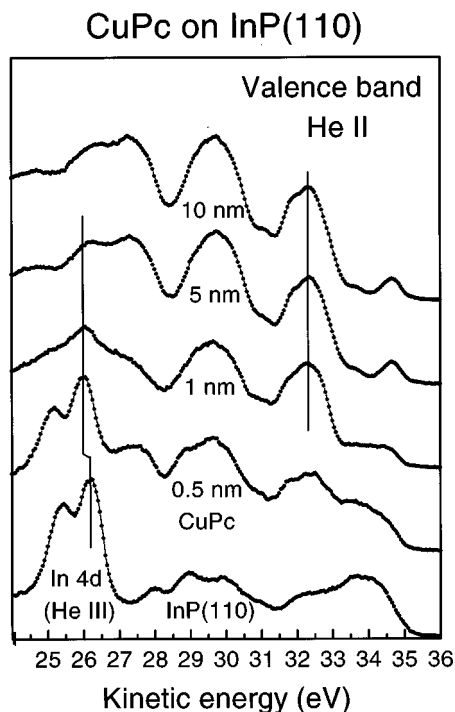
CuPc on InP(110)

FIG. 4. He II valence band and photoemission onset for increasing thickness of CuPc on InP(110). The vertical lines at 32.3 eV indicate the absence of band bending in CuPc. The broken line on the In core level shows the organic-induced band bending in InP.

InP valence band top higher than the top of the α-NPD HOMO.

The sudden shift of the photoemission onset upon deposition of the organic layer (left parts of Figs. 2 and 3) suggests the formation of an interface dipole barrier. The shift is equal to 0.7 ± 0.15 eV following the deposition of 4.5 nm α-NPD. The correction for band bending leads to an interface dipole barrier of 0.4 ± 0.15 eV (Fig. 6) with the InP vacuum level above that of the organic, suggesting a negative charge transfer from α-NPD to InP.

B. CuPc

The valence band spectra corresponding to incremental depositions of CuPc on InP are shown in Fig. 4. The molecular peaks are identifiable with 0.5 nm CuPc, but the InP spectral features, in particular near the top of the valence band, are not entirely eliminated until the coverage exceeds 10 nm. This could be due to a reduced sticking coefficient for CuPc on InP, or to inhomogeneities in the early stages of organic film growth. The CuPc HOMO peak is fully developed for thicknesses exceeding 1 nm. The 5 and 10 nm spectra are in excellent agreement with data obtained in a recent investigation of CuPc interfaces.[11] IE^{CuPc} is equal to 4.95 ± 0.15 eV, also in very good agreement with these data.

The In $4d$ core level shifts by 0.20 ± 0.05 eV toward higher binding energy (Fig. 5), indicating a downward band bending in the substrate due to the deposition of the first 0.5 nm CuPc. No additional band bending is recorded for larger CuPc coverage (Fig. 4). The absence of molecular level shifts in the 1, 5, and 10 nm spectra indicates that no band bending occurs in CuPc. The valence level offset between
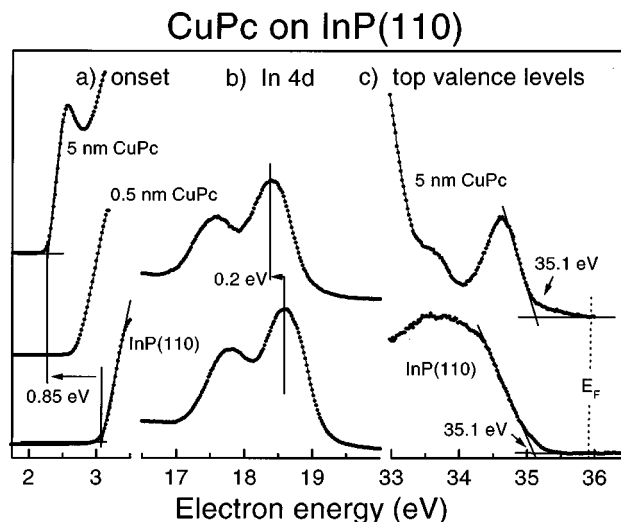
CuPc on InP(110)

FIG. 5. Photoemission onset, In $4d$ core level, and top of the valence states as a function of CuPc thickness on InP(110).

InP and CuPc, following correction for InP band bending, is 0.2 ± 0.1 eV. Unlike in the α-NPD case, the HOMO of the organic film is above the InP valence band top. Finally, the onset of photoemission is seen to shift toward lower energy with CuPc deposition (Fig. 5). The final shift, obtained with 5 nm CuPc and corrected for band bending gives a dipole barrier of 0.65 ± 0.15 eV, with E_{VAC}^{InP} above E_{VAC}^{CuPc} (Fig. 6), suggesting for this interface again a negative charge transfer from the organic solid to InP.

IV. DISCUSSION

It has been widely assumed that relative energy positions across interfaces involving molecular solids would be defined by the alignment of the vacuum levels of the two solids. This assumption was based on the presumed noninteractive nature of such interfaces due to the closed shell properties of molecules and the weak van der Waals bonds linking molecules to other solids. This assumption, however, was shown to be wrong for metal-organic interfaces where
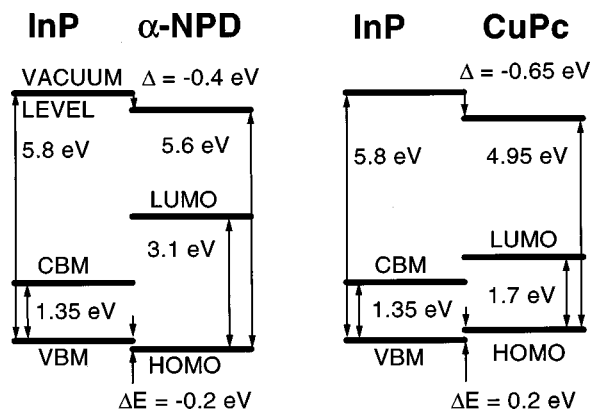

FIG. 6. Energy level diagram of the α-NPD/InP(110) and CuPc/InP(110) interfaces. VBM and CBM denote the valence band maximum and conduction band minimum of InP, respectively, while HOMO and LUMO represent the highest occupied and lowest unoccupied orbitals of the molecular compounds, respectively.
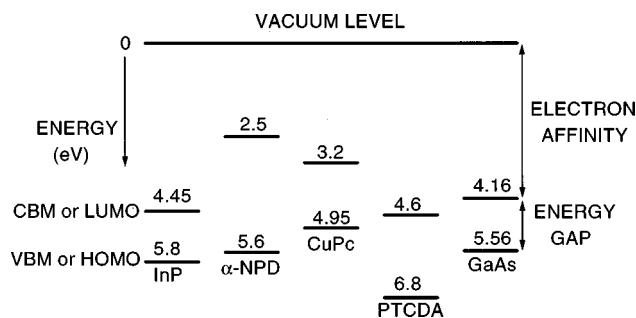
FIG. 7. VBM or HOMO, and CBM or LUMO, relative to a common vacuum level. These level diagrams represent the individual, separate materials.

dipole barriers in excess of 1 eV have been recorded.[4,9] The assumption was also shown to be wrong for several organic-organic heterojunctions, although dipoles at these interfaces were generally found to be smaller than at metal-organic interfaces, reaching 0.5 eV for organic pairs like Alq_3/PTCDA[10,14] and PTCDA/CuPc.[15] Bond polarization between molecules with different electron affinities, image charges at metal-organic interfaces, and geometric configurations of dipolar molecules at the interface have been invoked to justify a phenomenon which, to date, remains mostly not understood.

The results of the present investigation on the interface dipole and valence level alignment are summarized in Fig. 6. The interface dipole barrier is large in both cases, and its sign suggests a displacement of negative charge toward the inorganic semiconductor. This is opposite to the case of the PTCDA/GaAs interface where E_{VAC}^{PTCDA} is 0.5 eV above E_{VAC}^{GaAs}.[12] The impact of the dipole barrier on the energetics of the interface is significant. In the α-NPD/InP case, it inverts the sign of of the valence offset by moving the HOMO from 0.2 above to 0.2 eV below the InP valence band top. In the CuPc case, it reduces the offset from 0.85 eV (more than half of the InP gap) to 0.2 eV.

The sign of the dipole barrier can be understood in a qualitative way by comparing the IE and electron affinity of the various solids (Fig. 7). The former is measured by photoemission spectroscopy. The latter is obtained by subtracting the energy gap from the former to define to lowest unoccupied molecular orbital (LUMO). The optical band gap is used for the organics, i.e., 3.1 eV for α-NPD and 1.7 eV for CuPc. Figure 7 shows that the ionization energy and electron affinity of both α-NPD and CuPc are smaller than those of InP, suggesting that each molecule acts as a ''donor'' on the InP surface, consistent with a (partial) electron transfer from the molecule to the substrate. On the other hand, the ionization energy and electron affinity of PTCDA are larger than those of GaAs, suggesting that the molecule acts as an ''acceptor'' on that surface, consistent with the sign of the barrier observed at that interface.[12] PTCDA is expected to behave similarly on the InP surface.

A staggered band alignment is observed in the CuPc/InP(110) case, whereas a nested configuration is obtained at

the α-NPD/InP(110) interface (Fig. 6). Because of the barrier between the InP conduction band minimum and the LUMO of the organic film, neither configuration favors electron transfer from the inorganic semiconductor to the molecular film. The valence level offsets, however, are favorable for hole injection from the organic layer into InP (no barrier for α-NPD, small barrier for CuPc). α-NPD and CuPc are hole transport materials that could be used for injection without the requirement of making an ohmic contact to InP. Finally, an interesting, if not fortuitous, result is that the 0.5 eV HOMO offset measured at the all organic α-NPD/CuPc interface[11] is very close to the 0.4 eV HOMO offset obtained by transitivity from the present results. Transitivity in semiconductor heterojunction band offsets would suggest energy alignment mechanisms based on intrinsic levels e.g., charge neutrality levels, rather than on extrinsic mechanisms based on interface defects.

V. SUMMARY

We have presented a photoemission spectroscopy investigation of heterojunctions between InP(110) and two organic semiconductors, α-NPD and CuPc. Both interfaces exhibit dipole barriers that demonstrate the breakdown of the vacuum level alignment rule, and suggest a displacement of negative charge from the organic to the inorganic semiconductor. The direction of the charge displacement is consistent with the relative electron affinities and ionization energies of the solids. Finally, the ''valence band offset'' favors hole injection from the organic to the inorganic semiconductor at both heterojunctions.

ACKNOWLEDGMENTS

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