

Charge injection barrier and interface dipole formation in pentacene/semimetal heterostructures

Richard C. Hatch, Casey W. Sanchez, and Hartmut Höchst

Citation: *Appl. Phys. Lett.* **97**, 093303 (2010); doi: 10.1063/1.3486166

View online: <http://dx.doi.org/10.1063/1.3486166>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v97/i9>

Published by the [American Institute of Physics](#).

Related Articles

Electrical transport across Au/Nb:SrTiO₃ Schottky interface with different Nb doping
[Appl. Phys. Lett.](#) **100**, 213502 (2012)

Annealing dependence of diamond-metal Schottky barrier heights probed by hard x-ray photoelectron spectroscopy
[Appl. Phys. Lett.](#) **100**, 201606 (2012)

Modeling charge transfer at organic donor-acceptor semiconductor interfaces
[APL: Org. Electron. Photonics](#) **5**, 109 (2012)

Modeling charge transfer at organic donor-acceptor semiconductor interfaces
[Appl. Phys. Lett.](#) **100**, 203302 (2012)

Impacts of image force on the Schottky barrier height at metal-carbon nanotube contacts
[Appl. Phys. Lett.](#) **100**, 173104 (2012)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast

www.goodfellowusa.com

Charge injection barrier and interface dipole formation in pentacene/semimetal heterostructures

Richard C. Hatch,¹ Casey W. Sanchez,² and Hartmut Höchst^{1,a)}

¹Synchrotron Radiation Center, University of Wisconsin-Madison, 3731 Schneider Dr. Stoughton, Wisconsin 53589, USA

²Department of Physics, California State University, Fullerton, P.O. Box 6866, Fullerton, California 92843, USA

(Received 8 June 2010; accepted 15 August 2010; published online 3 September 2010)

Heterostructures containing pentacene (Pn) and the semimetals Bi and Sb were grown using molecular beam epitaxy. We used photoemission spectroscopy to measure the evolution of the vacuum level, hole-injection barrier, interface dipole, and work function changes as a function of Pn and semimetal coverage. The energy levels of the semimetal/Pn/semimetal sandwich structures show symmetric final values. The Pn/semimetal interfaces are very abrupt and established after a single monolayer ($\sim 15 \text{ \AA}$), whereas the semimetal/Pn interfaces extend over $\sim 100 \text{ \AA}$. © 2010 American Institute of Physics. [doi:10.1063/1.3486166]

With characteristics making them strong candidates for unique electronic devices, organic semiconductors (OSC) are currently the focus of much research.^{1,2} Due to its high field-effect mobility, pentacene (Pn) is one of the most promising conjugated oligomers used as active material in organic electronics.³ The characteristics of the interfaces between the conducting layers and OSCs have a very strong influence on the current-voltage characteristics. In these devices, the material interfaces are of great importance for charge transport. Because the interface properties have such a strong influence on device characteristics, it is desirable to understand and control the formation and quality of the various junctions present in metal/organic structures.

In this paper, we present angle resolved photoemission spectroscopy (ARPES) studies concerning the evolution and buildup of Bi/Pn/Bi, Sb/Pn/Sb, and Pn/Si(111)- 7×7 heterostructures. Photoemission spectroscopy was used to probe the electronic properties of the interface formation, and to monitor changes in work function Φ , ionization energy and vacuum level (VL), and to measure hole injection barriers (HIBs) and interface dipole (ID) formations at the interfaces. Interface studies⁴⁻⁶ have been reported for Pn/metal structures where the metal-organic bonds cause an initial planar adsorption geometry,⁷ accompanied in many cases by a change in morphology as films get thicker. An interesting situation arises, however, when molecules are deposited on a surface where the valence charge density is significantly reduced such as in semimetals.⁷ It has been shown that the reduced valence charge density favors Pn molecules to grow in a standing up fashion while still commensurate with the substrate and no change in film morphology occurs with increasing thicknesses.⁷⁻¹² Over the past few years, crystalline Pn films of high quality were grown on Bi substrates which were used in a variety of experiments exploring some basic electronic properties of Pn crystals.¹³⁻¹⁶

We report experiments performed on *in situ* grown heterostructures at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. Film thicknesses were calibrated using a quartz crystal microbalance. All films were

grown with the sample held at room temperature (RT) with the exception of Pn deposition on Bi. In this case the Bi substrate was held at 350 K which was reported to improve crystallinity of the Pn film.¹² Prior to Pn deposition single crystal Bi films were grown on Si(111)- 7×7 with details found elsewhere.¹⁴ Growth of Pn on Sb substrates not at RT was not explored. The photoemission experiments were performed with a total energy resolution of $\Delta E \sim 50 \text{ meV}$ for all experiments. A negative bias voltage was applied to the sample in order to measure changes in the low energy secondary electron cutoff (SEC). Referenced to the Fermi level, with a binding energy of $E_B = 0$, the VLs can be determined from the spectra by adding the photon energy to the negative binding energy of the SEC. The change in VL, ΔVL , is equal to the change in the SEC.

Figure 1 summarizes the evolution of the SEC for the Pn/Bi interface for various Pn thicknesses δ_{Pn} . This shows that the VL shifts rapidly for thicknesses up to $\delta_{\text{Pn}} \sim 15 \text{ \AA}$ after which very little shift is observed. The change in VL has been attributed to the formation of an ID.¹⁷ This ID is most likely caused by one of three things. First, a charge transfer, second, a quantum dipole from the Pn into the metal (a molecular dipole is not possible since Pn lacks a perma-

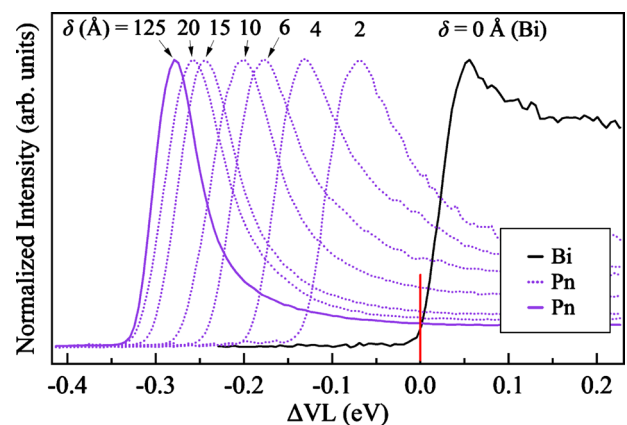


FIG. 1. (Color online) VL shift, ΔVL , as determined from the SECs. The vertical line indicates the cutoff location for the Bi substrate determined by the commonly accepted linear extrapolation method.

^{a)}Electronic mail: hhochst@wisc.edu.

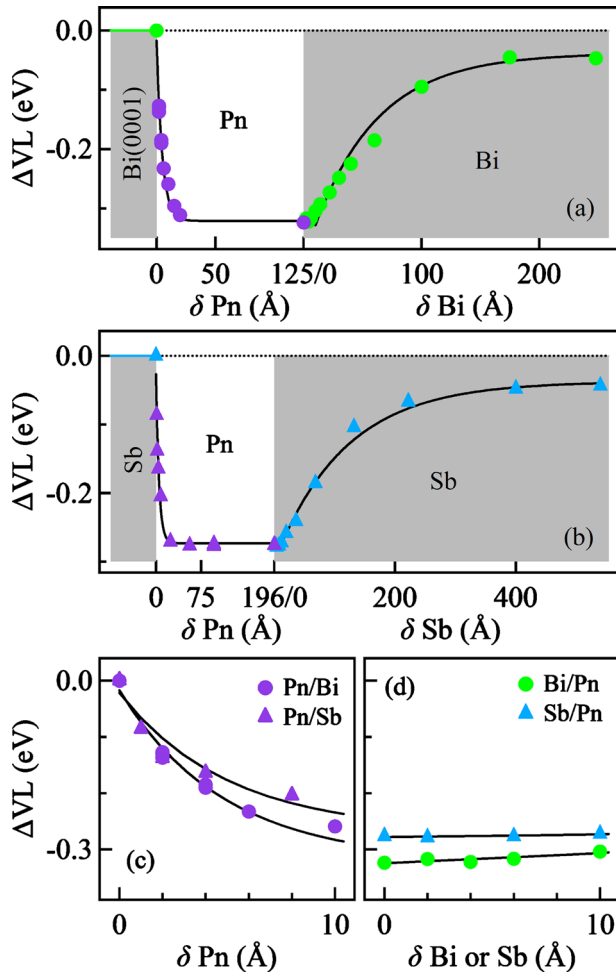


FIG. 2. (Color online) The change in VL (ΔVL) for Pn/Bi heterostructures (a) and Pn/Sb heterostructures (b). The evolution of the VL displays exponential behavior with the corresponding fit shown in black. The Pn/semimetal interfaces are abrupt and develop in ~ 10 Å as seen in (c), and contrast with the semimetal/Pn interfaces (d) which extend over ~ 100 Å. The VLs of the semimetal overlayers very nearly reach those of the semimetal substrates.

nent dipole) and third, the electron cloud of the adsorbed Pn molecules compresses the surface dipole of the substrate.¹⁸ The third case does not necessarily mean that an interfacial dipole is created but rather a modification of the existing surface dipole. Given the monolayer thickness of Pn on Bi of ~ 15 Å,⁹ the thickness dependence of the VL supports the idea that the ID primarily involves the first organic monolayer.

The evolution of the VL of the Pn/Sb and Pn/Si(111)- 7×7 structures behaves similarly to that of Pn/Bi(0001) with the VL shifting rapidly for the first ~ 15 Å and very little thereafter [see Figs. 2(a)–2(c)]. The extent to which the VL shifts depends on the Pn substrate with ID = 480 meV, 320 meV, and 280 meV for Si, Bi, and Sb substrates, respectively. In contrast to Bi, Sb does not grow epitaxially on Si(111)- 7×7 which results in a rougher film surface. The additional roughness increases the average molecule/substrate distance and reduces the pushback effect resulting in a smaller ID. Also seen in Figs. 2(a) and 2(b) is the exponential behavior with $\Delta VL \sim \exp(-\delta/\lambda_{\text{eff}})$. Fitting ΔVL for the various Pn films gives a $\lambda_{\text{eff}} = 5$ Å for both Bi(0001) and Sb substrates and a $\lambda_{\text{eff}} = 1$ Å for Si(111)- 7×7 substrates. The notion that the Pn/inorganic in-

terfaces are abrupt without a mixing of the Pn molecules with the substrate is supported by these λ s having values less than the Pn monolayer (ML) thickness (1 Pn ML is ~ 15 Å). Further evidence of an abrupt interface was reported previously by measuring the attenuation of Bi $5d_{5/2}$ electrons as a function of Pn coverage.¹²

The VL evolution of the semimetal/Pn interfaces is drastically different compared to that of the Pn/semimetal systems as one can see in Figs. 2(c) and 2(d). Virtually no change in VL is observed for the first 10 Å of Bi and Sb deposition. The constancy of the VL is in strong contrast to other metal/Pn systems where large and immediate shifts are observed.^{6,19,20} After an initial Bi or Sb coverage of $\delta \sim 10$ Å the VL begins to shift to higher energies, but much more gradually than for the Pn/semimetal case. The VL again has exponential behavior (after the initial 10 Å lag) and resulting fits to the data give $\lambda_{\text{eff}} = 55$ Å and 115 Å for Bi and Sb overlayers, respectively. In the semimetal/Pn case, the λ s are much greater than the Bi and Sb monolayer thickness and is most likely due to diffusion of the semimetal adatoms into the Pn film. The VL very nearly reaches that of the pure Bi and Sb surfaces resulting in Bi and Sb Φ s only ~ 50 meV smaller for the overlayer compared to those of the Bi or Sb substrates. This small deviation can be attributed to nonepitaxial growth with a surface lacking the spill-out component of the work function. A small amount of Pn may also float on the semimetal overlayers [similar to what has been reported for Ag, Au, and Cu (Ref. 21)] and serve to lower the Φ . The resulting IDs for the semimetal/Pn systems are ID = 280 meV and 230 meV for Bi and Sb, respectively.

It is interesting that the energy levels of the Bi/Pn/Bi and Sb/Pn/Sb heterostructures are so symmetric—equaling, or just surpassing, the symmetry of Ca/Pn/Ca (Ref. 6) and Sm/Pn/Sm (Ref. 20) heterostructures and in strong contrast to Au/, Ag/, Co/, and Cu/Pn systems.^{6,19–21} The fact that the Pn/Bi and Pn/Sb interfaces are electronically symmetric is surprising since this type of symmetry is generally observed with reactive metal/organic material interfaces as opposed to noble metal/organic interfaces.^{22–24}

In addition to tracking the evolution of the VL, the HIBs for the Pn/inorganic interfaces were determined by linear extrapolation of the highest occupied molecular orbital onset to the background. The HIBs determined for Pn/Bi, /Si(111)- 7×7 and /Sb interfaces were found to be HIB = 1.06 eV, 0.80 eV and 0.61 eV, respectively. A summary of how the HIBs and IDs depend on metal work function is shown in Fig. 3 where they are also compared to previously published values for Pn/metal heterostructures.^{5,6,18,20,25–27} In the Schottky limit, the slope of the HIBs should be $S_{\text{Schottky}} = -1$. Both the HIBs and the IDs have a linear dependence on the metal Φ , but the data do not support a true Schottky system. The deviation from the Schottky limit can be explained by the presence of a surface ID. Furthermore, it has been theoretically predicted that the ID also varies linearly with metal Φ .²⁸ In systems where there is a partial pinning of the Fermi level due to the presence of a surface dipole the equation $|S_{\text{HIB}}| + |S_{\text{ID}}| = 1$ should be valid and has indeed been reported for several organic/metal systems.²⁹ Fitting the data with the constraint that $|S_{\text{HIB}}| + |S_{\text{ID}}| = 1$ results in slopes of $S_{\text{HIB}} = -0.51 \pm 0.03$ and $S_{\text{ID}} = -0.49 \pm 0.03$ and the resulting fit is shown as black

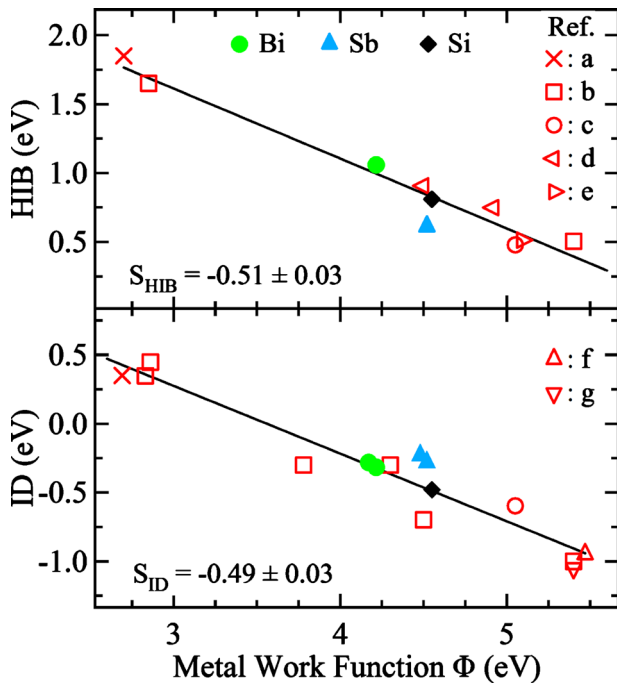


FIG. 3. (Color online) The HIB and ID of the Pn/Bi, /Sb, and /Si(111)-7 \times 7 heterostructures vs the “metal” work function Φ . Also shown are the IDs and HIBs of other Pn/inorganic heterostructures (a) Ref. 20, (b) Ref. 6, (c) Ref. 25, (d) Ref. 5, (e) Ref. 26, (f) Ref. 18, and (g) Ref. 27. Both the HIBs and the IDs of the Pn/metal heterostructures have a linear dependence on Φ and can be fit (black lines) such that $|S_{\text{ID}}| + |S_{\text{HIB}}| = 1$, where S_{ID} and S_{HIB} are the slopes of the HIB and ID, respectively.

lines in Fig. 3. Fitting the HIB and ID data separately does not noticeably improve the quality of the fit nor does it alter S_{HIB} or S_{ID} .

In conclusion, the Pn/semimetal interfaces are atomically abrupt ($\lambda_{\text{eff}} \sim 5 \text{ \AA}$) and there is no diffusion of the Pn into the semimetal substrate. The semimetal/Pn interfaces, however, extend over $\sim 100 \text{ \AA}$ and are most likely due to diffusion of the semimetal into the Pn substrate. The Pn/semimetal heterostructures are found to be highly symmetric at both sides of the interface. The HIBs and IDs vary linearly with metal Φ with a slope of ~ -0.5 as predicted by theory.²⁸

We acknowledge David L. Huber for discussions. The SRC, University of Wisconsin-Madison, and the SRC-Research Experiences for Undergraduates (REU) Program

are supported by the National Science Foundation under Award No. DMR-0537588.

- ¹S. R. Forrest, *Nature (London)* **428**, 911 (2004).
- ²T. Sekitani, M. Takamiya, Y. Noguchi, S. Nakano, Y. Kato, T. Sakurai, and T. Someya, *Nature Mater.* **6**, 413 (2007).
- ³D. J. Gundlach, Y. Y. Lin, T. N. Jackson, S. F. Nelson, and D. G. Schlom, *IEEE Electron Device Lett.* **18**, 87 (1997).
- ⁴C. Baldacchini, C. Mariani, M. G. Betti, L. Gavioli, M. Fanetti, and M. Sancrotti, *Appl. Phys. Lett.* **89**, 152119 (2006).
- ⁵B. Jaeckel, J. B. Sambur, and B. A. Parkinson, *J. Appl. Phys.* **103**, 063719 (2008).
- ⁶N. J. Watkins, L. Yan, and Y. Gao, *Appl. Phys. Lett.* **80**, 4384 (2002).
- ⁷G. E. Thayer, J. T. Sadowski, F. Meyer zu Heringdorf, T. Sakurai, and R. M. Tromp, *Phys. Rev. Lett.* **95**, 256106 (2005).
- ⁸A. Al-Mahboob, J. T. Sadowski, Y. Fujikawa, K. Nakajima, and T. Sakurai, *Phys. Rev. B* **77**, 035426 (2008).
- ⁹J. T. Sadowski, T. Nagao, S. Yaginuma, Y. Fujikawa, A. Al-Mahboob, K. Nakajima, T. Sakurai, G. E. Thayer, and R. M. Tromp, *Appl. Phys. Lett.* **86**, 073109 (2005).
- ¹⁰A. Al-Mahboob, J. T. Sadowski, T. Nishihara, Y. Fujikawa, Q. K. Xue, K. Nakajima, and T. Sakurai, *Surf. Sci.* **601**, 1304 (2007).
- ¹¹J. T. Sadowski, G. Sasaki, S. Nishikata, A. Al-Mahboob, Y. Fujikawa, K. Nakajima, R. M. Tromp, and T. Sakurai, *Phys. Rev. Lett.* **98**, 046104 (2007).
- ¹²R. C. Hatch and H. Höchst, *Surf. Sci.* **604**, 1684 (2010).
- ¹³R. C. Hatch, D. L. Huber, and H. Höchst, *Phys. Rev. Lett.* **104**, 047601 (2010).
- ¹⁴R. C. Hatch, D. L. Huber, and H. Höchst, *Phys. Rev. B* **80**, 081411 (2009).
- ¹⁵H. Kakuta, T. Hirahara, I. Matsuda, T. Nagao, S. Hasegawa, N. Ueno, and K. Sakamoto, *Phys. Rev. Lett.* **98**, 247601 (2007).
- ¹⁶M. Muntwiler, Q. Yang, W. A. Tisdale, and X. Y. Zhu, *Phys. Rev. Lett.* **101**, 196403 (2008).
- ¹⁷H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* **11**, 605 (1999).
- ¹⁸P. G. Schroeder, C. B. France, J. B. Park, and B. A. Parkinson, *J. Appl. Phys.* **91**, 3010 (2002).
- ¹⁹M. Popinciuc, H. T. Jonkman, and B. J. v. Wees, *J. Appl. Phys.* **100**, 093714 (2006).
- ²⁰N. Koch, J. Ghijsen, R. L. Johnson, J. Schwartz, J. J. Pireaux, and A. Kahn, *J. Phys. Chem. B* **106**, 4192 (2002).
- ²¹B. Jaeckel, J. B. Sambur, and B. A. Parkinson, *Langmuir* **23**, 11366 (2007).
- ²²F. Faupel, R. Willecke, and A. Thran, *Mater. Sci. Eng. R.* **22**, 1 (1998).
- ²³A. Rajagopal and A. Kahn, *J. Appl. Phys.* **84**, 355 (1998).
- ²⁴C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **89**, 449 (2001).
- ²⁵F. Amy, C. Chan, and A. Kahn, *Org. Electron.* **6**, 85 (2005).
- ²⁶L. Diao, C. D. Frisbie, D. D. Schroepfer, and P. P. Ruden, *J. Appl. Phys.* **101**, 014510 (2007).
- ²⁷N. Koch, A. Kahn, J. Ghijsen, J. J. Pireaux, J. Schwartz, R. L. Johnson, and A. Elschner, *Appl. Phys. Lett.* **82**, 70 (2003).
- ²⁸R. T. Tung, *Phys. Rev. Lett.* **84**, 6078 (2000).
- ²⁹I. G. Hill, A. Rajagopal, A. Kahn, and Y. Hu, *Appl. Phys. Lett.* **73**, 662 (1998).