

Effect of phosphonic acid surface modifiers on the work function of indium tin oxide and on the charge injection barrier into organic single-layer diodes

Asha Sharma, Andreas Haldi, Peter J. Hotchkiss, Seth. R. Marder, and Bernard Kippelen

Citation: *J. Appl. Phys.* **105**, 074511 (2009); doi: 10.1063/1.3095490

View online: <http://dx.doi.org/10.1063/1.3095490>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v105/i7>

Published by the [American Institute of Physics](http://www.aip.org).

Additional information on J. Appl. Phys.

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

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

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

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

ADVERTISEMENT



The advertisement banner features a green and white background with abstract, flowing lines. On the left, the text "AIP Advances" is displayed in a green, sans-serif font, with a series of orange and yellow circles of varying sizes arranged in a curved path above the word "Advances". On the right, there is a circular seal with a white border containing the text "Now Indexed in Thomson Reuters Databases". Below this, a dark blue horizontal bar contains the text "Explore AIP's open access journal:" in white, followed by a list of three bullet points in white text.

AIP Advances

Now Indexed in Thomson Reuters Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

Effect of phosphonic acid surface modifiers on the work function of indium tin oxide and on the charge injection barrier into organic single-layer diodes

Asha Sharma,¹ Andreas Haldi,¹ Peter J. Hotchkiss,² Seth. R. Marder,² and Bernard Kippelen^{1,a)}

¹Center for Organic Photonics and Electronics (COPE), School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

²Center for Organic Photonics and Electronics (COPE), School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

(Received 17 December 2008; accepted 3 February 2009; published online 9 April 2009)

We investigate the use of several phosphonic acid surface modifiers in order to increase the indium tin oxide (ITO) work function in the range of 4.90–5.40 eV. Single-layer diodes consisting of ITO/modifier/*N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4'' diamine (α -NPD)/Al and ITO/modifier/pentacene/Al were fabricated to see the influence of the modified ITO substrates with different work functions on the charge injection. To calculate the charge injection barrier with different surface modifiers, the experimentally measured current density-voltage (J - V) characteristics at different temperatures are fitted using an equivalent circuit model that assumes thermionic emission across the barrier between the ITO work function and the highest occupied molecular orbital of the organic material. The charge injection barrier height extracted from the model for various surface modifier-based diodes is independent of the ITO work function within the range of changes achieved through modifiers for both α -NPD and pentacene-based single-layer diodes. © 2009 American Institute of Physics. [DOI: 10.1063/1.3095490]

I. INTRODUCTION

In organic electronic devices, the injection of holes and electrons from the electrodes into the organic semiconductors is a key issue for their efficient operation.^{1,2} Therefore, the optimization of the electrodes and the understanding of the interface characteristics have been the subject of investigation in previous studies.^{3–6} For efficient hole or electron injection, the barrier height between the work function of the electrode and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of a given organic material, respectively, should be minimized. To achieve this goal, several studies have been reported in the past where the interfaces on both electrodes, the anode and cathode, have been modified.^{7–12} Indium tin oxide (ITO) is a transparent conducting electrode often used as the anode to inject holes into organic semiconductors. However, the relatively low work function of untreated ITO results in a significant barrier at the interface for hole injection into the HOMO level of most organic semiconductors. Modifying the ITO anode to raise the work function has been investigated in the past by various approaches such as plasma (air, Ar, oxygen, SF₆) treatment, UV ozone treatment, use of a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) intrinsically conducting polymer layer, or by use of metal oxide nanoparticles.^{13–20} Alternatively, it has been shown that the use of dipolar molecules on the ITO surface can also increase the work function as a result of the orientation of the mo-

lecular dipoles.^{21–24} Binding groups such as silanes, siloxanes, benzene derivatives with different groups (–COCl, –SO₂Cl, and PO₂Cl₂), and phosphonic acids have all been used to bind to the ITO surface and improve the performance of organic electronic devices.^{24–28} While most of these reports focus on the improved performance of devices with such interface modifiers, little is devoted to the influence of the surface modifiers on the charge injection in terms of barrier heights and consequently on the current/voltage characteristics.

In this paper, we investigate the use of various surface modifiers based on phosphonic acid binding groups to modify the ITO work function, and we study the charge injection effects in single-layer diodes fabricated from two model hole transport organic semiconductors with different HOMO energy levels: *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4'' diamine (α -NPD) (5.4 eV) and pentacene (4.9 eV). To establish a correlation between the experimentally measured work function due to the surface modifiers and the charge injection barrier in the diode, we modeled the experimentally measured current density-voltage (J - V) characteristics with an equivalent circuit model proposed previously,²⁹ in which thermionic emission across the barrier from the anode into the organic semiconductor is assumed.

II. EXPERIMENTAL

The chemical structures of the phosphonic acid surface modifiers employed in the ITO modification are shown in Fig. 1. Phosphonic acids were synthesized as reported previously.³⁰ ITO coated glass substrates (20 Ω/\square Colorado Concept Coatings, L.L.C.) were first cleaned in an ultrasonic

^{a)}Author to whom correspondence should be addressed. Electronic mail: kippelen@ece.gatech.edu.

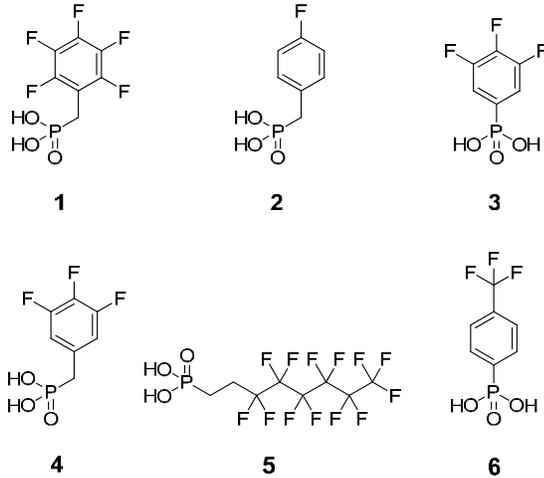


FIG. 1. Chemical structures of various phosphonic acid surface modifiers used to modify ITO.

bath using a dilute solution of Triton-X (Aldrich) in deionized (DI) water (20 min) followed by a final ultrasonication for 20 min in DI water. Further organic cleaning was done in the ultrasonic bath using acetone and ethanol for 20 min each. Cleaned ITO substrates were then dried in a vacuum oven at 70 °C under a pressure of (1×10^{-2} Torr) for 1 h. The surface modification was performed in a glove box filled with N_2 having O_2 and H_2O level <20 and <1 ppm, respectively, by dipping the cleaned ITO substrates in a solution of the phosphonic acid (1 mM in $CHCl_3:C_2H_5OH:2:1$) for 30 min, followed by annealing at 120 °C (1 h). The work function of the ITO samples was measured in air using a Kelvin probe (Besocke Delta Phi). Prior to each measurement, the gold reference electrode (3 mm diameter grid) was calibrated with a highly oriented pyrolytic graphite surface.

For the study of charge injection effects from the modified ITO electrode into the organic layer, single-layer diodes with the structure ITO/modifier/ α -NPD (120 nm)/Al and ITO/modifier/pentacene (100 nm)/Al were fabricated using thermal evaporation. α -NPD and pentacene were thermally evaporated at the rate of 1 and 0.6 Å/s, respectively, and at a pressure below 1×10^{-7} Torr. Finally, an Al cathode (200 nm) was deposited at a rate of 2 Å/s. An active area of ~ 0.1 cm² per device was obtained by using a shadow mask. The devices were tested inside a glove box under nitrogen. For temperature dependent measurements, the devices were kept in a copper holder in contact with a temperature controlled stage.

III. INJECTION BARRIER DETERMINATION IN SINGLE-LAYER DIODES

To extract the charge injection barrier for different surface modifiers the temperature dependent J - V characteristics for the diodes based on several modifiers were measured. The experimentally measured J - V curves were fitted using a previously proposed equivalent circuit model.²⁹ The equivalent circuit diagram with its device parameters under consideration is shown in the inset of Fig. 4 for the α -NPD diode. The magnitude of the current density in these devices can be

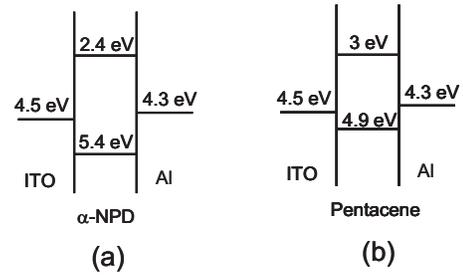


FIG. 2. Approximate energy structure of single-layer diodes with geometry (a) ITO (unmodified)/ α -NPD/Al, and (b) ITO (unmodified)/pentacene/Al to test the charge injection barrier among different surface modifiers on ITO. The energy values for α -NPD in (a) are taken from Ref. 32, and the energy values for pentacene in (b) are taken from Ref. 33.

described by the injection barrier across the interface and the transport through the bulk of the organic material. The current density due to the injection of charges across the barrier between the work function of the ITO anode and the HOMO level of the α -NPD can be explained by the Schottky model for thermionic injection. The relationship between the Schottky emission current density J and the applied voltage V is given by

$$J = J_0 \left(\exp \left[\frac{qV}{nkT} \right] - 1 \right), \quad (1)$$

$$J_0 = A^* T^2 \exp \left(- \frac{\Phi_B}{kT} \right). \quad (2)$$

In the above equations, J_0 is the saturation current density, q is the elementary charge, n is the ideality factor of the diode, k is the Boltzmann constant, T is the temperature, A^* is the effective Richardson constant, and Φ_B is the injection barrier for charges. Furthermore, once charges have been injected they are transported through the bulk of the semiconductor, and the conduction in the bulk organic layer can be described by space-charge limited current (SCLC) as derived by Lampert and Mark,³¹

$$j_{SCLC} = \frac{9}{8} \epsilon \mu \exp \left(\beta \sqrt{\frac{V}{L}} \right) \frac{V^2}{L^3}, \quad (3)$$

$$\mu = \mu_0(T) \exp(\beta \sqrt{V/L}), \quad (4)$$

where μ is the charge mobility, $\mu_0(T)$ is the temperature dependent zero-field mobility, ϵ is the dielectric constant, L is the thickness of the sample, and β is the field-dependence factor of the mobility. Previously, we have validated this equivalent circuit model in detail for ITO/ α -NPD/Al diodes where various parameters could be extracted from the model.²⁹

IV. RESULTS AND DISCUSSION

A. Charge injection barrier in ITO/modifier/ α -NPD/Al diodes

The approximate energy diagrams of the single-layer diodes consisting of α -NPD and pentacene as organic layers are depicted in Figs. 2(a) and 2(b) (the energy values for α -NPD are taken from Ref. 32 and for pentacene from Ref.

TABLE I. Work function values for the modified ITO substrates using various phosphonic acid surface modifiers as measured by Kelvin probe. Additionally, the extracted zero-field mobility (μ_0) values at RT, the injection barrier height (Φ_B) and the effective Richardson constant (A^*), extracted from fits of the equivalent circuit model to temperature dependent current density-voltage (J - V) characteristics of ITO/modifier/ α -NPD/Al diodes using different surface modifiers are shown.

Surface modifier	Work function (eV)	μ_0 (RT) ($\text{cm}^2/\text{V s}$)	Φ_B (eV)	A^* ($\text{A}/\text{cm}^2 \text{K}^2$)
1	4.90 ± 0.05	$3.8 \pm 0.1 \times 10^{-4}$	0.94 ± 0.07	3.5×10^{-7}
2	4.91 ± 0.01	$2.8 \pm 0.2 \times 10^{-4}$	0.99 ± 0.03	2.2×10^{-6}
3	5.17 ± 0.02	$3.2 \pm 0.1 \times 10^{-4}$	1.13 ± 0.08	1.1×10^{-5}
5	5.30 ± 0.04	$3.0 \pm 1 \times 10^{-4}$	1.01 ± 0.08	1.8×10^{-6}
6	5.40 ± 0.05	$2.4 \pm 0.1 \times 10^{-4}$	1.22 ± 0.06	3.6×10^{-5}

^aWork function values are the average over three different locations on same substrate. The extracted μ_0 and Φ_B values are the average over three different devices fabricated in the same run.

33).^{32,33} First, the case of the diode structure with ITO/ α -NPD/Al geometry will be discussed. In the electronic energy diagram it can be assumed that the electron injection from the Al cathode is negligible in comparison to the hole injection from the ITO anode because of a large energy barrier height (1.9 eV) at the interface between Al (work function ~ 4.3 eV) and α -NPD (LUMO ~ 2.4 eV) than the energy barrier height (0.9 eV) between the ITO work function (4.5 eV) and the HOMO of α -NPD (5.4 eV). The unmodified ITO electrode yielded a measured work function value of 4.50 ± 0.02 eV. In order to impact the hole injection barrier at the ITO interface, modifications of the value of the work function of the ITO anode were achieved through the use of phosphonic acid surface modifiers. The work function values of the differently modified ITO substrates were measured using Kelvin probe and are shown in Table I. It can be seen that the work function of ITO can be increased by a large range (4.90–5.40 eV) by using phosphonic acid surface modifiers. This is due to the varying effective dipole moment at the ITO surface leading to different electrostatic potentials at the surface. With increasing ITO work function, it can be anticipated that the hole injection into the single-layer diode might be enhanced as a result of a reduced energy barrier between the ITO work function and the HOMO of α -NPD, shown in Fig. 2(a).

The room temperature J - V characteristics of the ITO/modifier/ α -NPD/Al diodes based on several surface modifiers (including unmodified ITO as reference) are compared in Fig. 3. The unmodified ITO anode, which has the lowest work function, exhibited the lowest current density in the diode structure. In contrast, the diodes based on ITO modified using modifiers pentafluorobenzylphosphonic acid (1), 4-fluorobenzylphosphonic acid (2) 3,4,5-trifluorophenylphosphonic acid (3), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylphosphonic acid (5), and 4-(trifluoromethyl)phenylphosphonic acid (6) give a higher charge injection. This is expected considering the higher work function of the ITO after modification with 1, 2, 3, 5, and 6 as compared to unmodified ITO. However, the current densities as a function of the applied voltage for the diodes incorporating ITO modified with 1, 2, 3, 5, or 6 appear to be

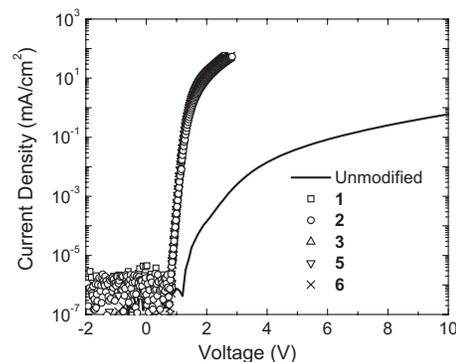


FIG. 3. Current density-voltage (J - V) characteristics at room temperature of the ITO/modifier/ α -NPD/Al diodes with various surface modifiers. The J - V characteristics of an unmodified ITO based diode are also shown for comparison.

similar despite a large variation in the anode work function. An air plasma-modified ITO based diode also exhibited J - V characteristics similar to these devices based on phosphonic acid-modified ITO.

For better understanding of the charge injection in such devices, temperature dependent J - V measurements were carried out. The results for a diode based on ITO modified with 1 are shown in Fig. 4. The experimentally measured J - V characteristics were fitted using the equivalent circuit model (shown in the inset of Fig. 4). It can be seen that the experimentally measured J - V characteristics at different temperatures for α -NPD based diodes are well fitted to the proposed model. Similarly good fits were obtained for the diodes utilizing other surface modifiers. However, for single-layer diodes with unmodified ITO, the temperature dependent J - V characteristics could not be measured due to a lack of repeatable measurements. This could be due to very high driving voltages for a diode based on unmodified ITO in comparison to the devices based on phosphonic acid-modified ITO (Fig. 3). From the J - V curves at room temperature, the extracted mobility values for different devices utilizing 1, 2, 3, 5, or 6 were all in the range of 10^{-4} $\text{cm}^2/\text{V s}$ (Table I). These values are in agreement with the mobility value determined previously (1.2×10^{-4}) from our model on air plasma-modified

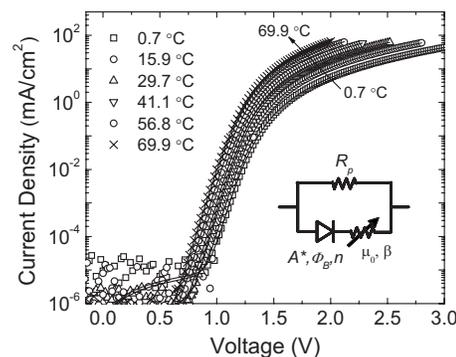


FIG. 4. J - V characteristics of ITO/modifier 1/ α -NPD/Al diodes measured at different temperatures ranging from 0.7 to 69.9 °C. Experimental data are shown in the symbols and the solid lines represent the simulated curve from the equivalent circuit model. The equivalent circuit showing various device parameters under consideration is shown in the inset.

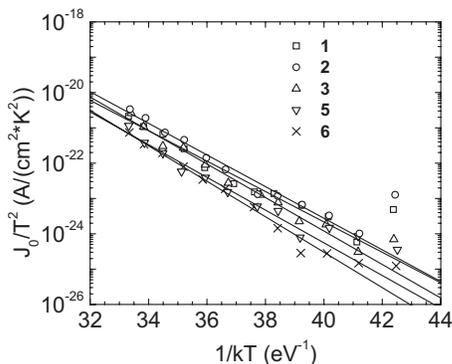


FIG. 5. $\log(J_0/T^2)$ vs $1/kT$ for ITO/modifier/ α -NPD/Al single-layer diodes utilizing different surface modifiers on ITO. The injection barrier (Φ_B) and the effective Richardson constant (A^*) can be obtained from the extrapolation of the linear fits to the data points. The experimental data are shown by the symbols for different modifiers and the solid lines are the fits to the data.

ITO based diode,²⁹ and also with independently measured values using time-of-flight or SCLC measurements in various reports.^{34,35}

To extract the injection barrier height, the temperature dependence of the current density can be analyzed according to the expressions shown in Eqs. (1) and (2). The linear relationship between $\log(J_0/T^2)$ and $1/T$ will determine the barrier height (Φ_B) which is the slope of curves as shown in Fig. 5 for ITO modified with different phosphonic acids. The slopes of the linear fits are constant regardless of the phosphonic acid used. The calculated injection barrier heights (Φ_B) between the modified ITO anodes and the HOMO of the α -NPD organic layer (averaged over three devices), and the effective Richardson constant (A^*) values are summarized in Table I. The values for the injection barrier height for the various surface modifiers are ~ 1 eV. The injection barrier, therefore, does not appear to be influenced by the work function changes in the ITO within the range of 4.90–5.40 eV as achieved using various organic surface modifiers.

B. Charge injection barrier in ITO/modifier/pentacene/Al diodes

Next, the case of diodes incorporating pentacene, which has a lower HOMO [4.9 eV, Fig. 2(b)] in comparison with α -NPD (HOMO, 5.4 eV), was considered. The room temperature J - V characteristics of ITO/modifier/pentacene/Al diodes are shown in Fig. 6. It can be seen that similar to the α -NPD based diodes, the J - V characteristics of pentacene-based diodes with different surface modifiers also show similar current densities at a given applied voltage. Hence, no charge injection enhancement seems to occur upon increasing the ITO work function. It should also be noted that diodes based on unmodified ITO exhibited similar current density as the diodes with surface modifiers. This is in contrast to the earlier observation with the α -NPD diodes where a device based on unmodified ITO exhibited a lower current density at a given applied voltage in comparison to those devices incorporating modified ITO diodes. To ensure that the injection barriers are in fact similar for the different ITO substrates, again the temperature dependent J - V characteris-

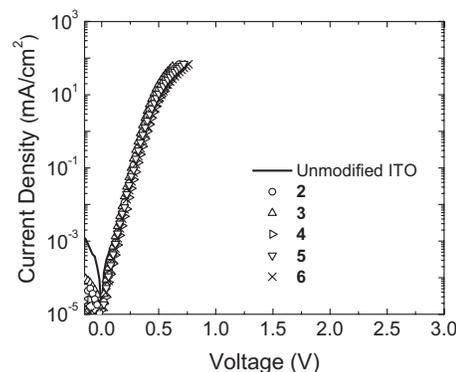


FIG. 6. Comparison of current density-voltage J - V characteristics at room temperature of the ITO/modifier/pentacene/Al diodes using different surface modifiers on ITO and an unmodified ITO based diode.

tics were measured for pentacene-based diodes with an unmodified ITO anode as well as ITO anodes modified with different phosphonic acids. Again, the experimentally measured J - V curves at different temperatures were fitted using the equivalent circuit model. It was important to take into account an Ohmic resistor instead of an SCLC resistor, as in the case of α -NPD, in the equivalent circuit model (see inset Fig. 7). Details of the model and the adjustment to the equivalent circuit model for treating low band-gap materials such as pentacene are described elsewhere.²⁹ Good fits were obtained for all the devices utilizing different surface modifiers at the ITO anode (the use of 5 is shown in Fig. 7 as an example). Again, the injection barrier height (Φ_B) for the holes can be derived from the slope between $\log(J_0/T^2)$ and $1/T$, as shown in Fig. 8 for different phosphonic acid surface modifiers in pentacene-based diodes. The calculated values of the injection barrier height (Φ_B) from the modified ITO into pentacene are summarized in Table II and are in the range of ~ 0.6 eV. Therefore, as in the case of the α -NPD diodes, pentacene diodes also show an invariance of the injection barrier height Φ_B from the work function of the ITO even over larger values. Hence, no charge injection enhancement effects could be observed.

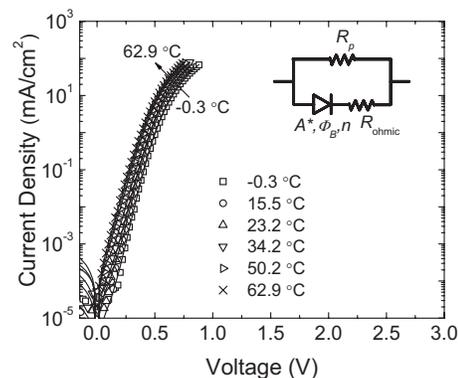


FIG. 7. Current density-voltage (J - V) characteristics of ITO/modifier 5/pentacene/Al diodes measured at different temperatures ranging from -0.3 to 62.9 °C. Experimental data are shown in the symbols and solid lines represent the simulated curve from the equivalent circuit model. The equivalent circuit showing various device parameters under consideration is shown in the inset.

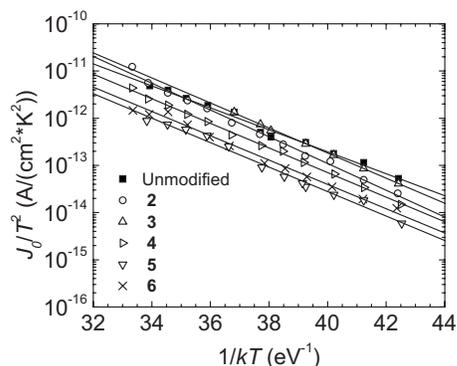


FIG. 8. $\text{Log}(J_0/T^2)$ and $1/kT$ for ITO/modifier/pentacene/Al single-layer diodes utilizing different surface modifiers on ITO and an unmodified ITO. The injection barrier (Φ_B) and the effective Richardson constant (A^*) can be obtained from the extrapolation of the linear fits to the data points. The experimental data are shown by the symbols for different modifiers and the solid lines are the fits to the data.

These rather unexpected results suggest that interfacial dipoles are formed on the modified ITO, which match the dipole moments of the modifiers and result in Fermi level pinning of the ITO work function with the HOMO energy levels of the organic layers. Fermi level pinning has been suggested in several other independent studies using ultraviolet photoelectron spectroscopy (UPS) relating to the metal/organic interfaces and the polymer/organic interfaces.^{36–39} These studies estimated the hole injection barriers for various interfaces formed between different organic semiconductors with varying HOMO and metal electrodes with different work function. For example, Fugukawa *et al.*³⁸ estimated the dependence of the hole injection barrier of pentacene films grown on substrates with different values of the work function. It was found that for a substrate with a work function smaller than the ionization potential (IP) of pentacene, the hole injection barrier decreases upon an increase in the substrate work function. However, when the work function of the substrate reaches values close to the HOMO energy, the hole injection barrier becomes independent of the work function despite a continuing variance of the work function by more than 1 eV. Similarly, Koch *et al.*³⁶ investigated the hole injection barrier of pentacene deposited

TABLE II. Work function values for the modified ITO substrates using various phosphonic acid surface modifiers measured by Kelvin probe. The extracted injection barrier height (Φ_B) and Richardson constant (A^*) for pentacene from fits of the equivalent circuit model to the temperature dependent J - V characteristics of ITO/modifier/pentacene/Al diodes using different surface modifiers.

Surface modifier	Work function (eV)	Φ_B (eV)	A^* (A/cm ² K ²)
Unmodified	4.50 ± 0.02	0.56 ± 0.04	3.9 × 10 ⁻⁴
2	4.91 ± 0.01	0.64 ± 0.03	2.4 × 10 ⁻²
3	5.17 ± 0.02	0.63 ± 0.03	7.6 × 10 ⁻³
4	5.20 ± 0.01	0.60 ± 0.04	1.9 × 10 ⁻³
5	5.30 ± 0.04	0.60 ± 0.04	6.4 × 10 ⁻⁴
6	5.40 ± 0.05	0.60 ± 0.03	8.4 × 10 ⁻⁴

^aWork function values are the average over three different locations on same substrate. The extracted injection barrier height (Φ_B) values are the average over three different devices fabricated in the same run.

onto substrates with different work function values. They also used UPS experiments to show that the hole injection barrier for pentacene remained unchanged even when the work function of the substrate was varied from 4.25 to 5.15 eV. These findings have been assigned to Fermi level pinning effects of the metal relative to IP of the pentacene due to the charge transfer at the interface. Though our results were obtained by a different experimental approach, they are in agreement with these findings. Remarkably, the calculated hole injection barrier heights of ~ 0.6 eV for pentacene on surface-modified ITO from the equivalent circuit model are close to the value of 0.5 ± 0.03 eV, as reported by Fugukawa *et al.*³⁸ for a pentacene film on ITO, and that (0.4 eV) reported by Koch *et al.*³⁶ on PEDOT:PSS-modified ITO from UPS studies.

In regard to the results obtained with α -NPD, Braun *et al.*³⁹ investigated the hole injection barrier height between this material and substrates with varying values of work function using UPS. They observed an invariance of the barrier height for α -NPD films when the work function of the substrate was varied from 4.9 to 5.9 eV. Again, these reported data are consistent with our findings that the hole injection barrier height in single-layer α -NPD diodes is invariant with work function changes in the ITO within the range of 4.90–5.40 eV achieved using various organic surface modifiers. However, the predicted values of the hole injection barrier (~ 1 eV) for α -NPD on the surface-modified ITO in the present study are higher in comparison to the earlier reported value (0.5 eV) estimated from the UPS studies for α -NPD on ITO.³⁹

V. SUMMARY

In summary, we have used several phosphonic acids to modify the surface of ITO substrates in order to tune the ITO work function between 4.90 and 5.40 eV. These differently modified ITO anodes have been used in α -NPD and pentacene-based single-layer diodes to study their impact on charge injection in a single-carrier device. The current densities at a given applied voltage are higher after the use of various surface modifiers in comparison to an unmodified reference ITO for the case of α -NPD diodes. However, no improvement can be seen in ITO/modifier/ α -NPD/Al diodes upon varying the work function between 4.90 and 5.40 eV by using phosphonic acids 1–6. The injection barrier height is calculated from the temperature dependent J - V characteristics using an equivalent circuit model. The calculated injection barrier height for hole injection is ~ 1 eV and is independent of the ITO work function within the surface modifiers for ITO/modifier/ α -NPD/Al diodes. For ITO/modifier/pentacene/Al diodes, no change was observed regardless of whether the ITO substrates were modified with phosphonic acids or not. A constant injection barrier height of ~ 0.6 eV was found in the case of pentacene diodes with or without modification of the ITO surface. The invariance of the injection barrier within the range of work function values obtained by ITO surface modification is tentatively assigned to Fermi level pinning effects as proposed in previous studies^{36–39} based on UPS experiments.

ACKNOWLEDGMENTS

This material is based upon work supported in part by Solvay S.A., by the STC Program of the National Science Foundation under Agreement No. DMR-0120967, and by the Office of Naval Research.

- ¹I. D. Parker, *J. Appl. Phys.* **75**, 1656 (1994).
- ²G. G. Malliaras and J. C. Scott, *J. Appl. Phys.* **83**, 5399 (1998).
- ³M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **64**, 085201 (2001).
- ⁴T. M. Brown and F. Cacialli, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 2649 (2003).
- ⁵J. C. Scott, *J. Vac. Sci. Technol. A* **21**, 521 (2003).
- ⁶H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater. (Weinheim, Ger.)* **11**, 605 (1999).
- ⁷J. Cui, Q. L. Huang, J. C. G. Veinot, H. Yan, Q. W. Wang, G. R. Hutchison, A. G. Richter, G. Evmenenko, P. Dutta, and T. J. Marks, *Langmuir* **18**, 9958 (2002).
- ⁸R. A. Hatton, M. R. Willis, M. A. Chesters, F. J. M. Rutten, and D. Briggs, *J. Mater. Chem.* **13**, 38 (2003).
- ⁹J. Lee, B. J. Jung, J. I. Lee, H. Y. Chu, L. M. Do, and H. K. Shim, *J. Mater. Chem.* **12**, 3494 (2002).
- ¹⁰T. M. Brown, R. H. Friend, I. S. Millard, D. J. Lacey, J. H. Burroughes, and F. Cacialli, *Appl. Phys. Lett.* **79**, 174 (2001).
- ¹¹M. Matsumura, T. Akai, M. Saito, and T. Kimura, *J. Appl. Phys.* **79**, 264 (1996).
- ¹²I.-H. Hong, M.-W. Lee, Y.-M. Koo, H. Jeong, T.-S. Kim, and O.-K. Song, *Appl. Phys. Lett.* **87**, 063502 (2005).
- ¹³J. S. Kim, M. Granström, R. H. Friend, N. Johansson, W. R. Salaneck, R. Daik, W. J. Feast, and F. Cacialli, *J. Appl. Phys.* **84**, 6859 (1998).
- ¹⁴B. Choi, H. Yoon, and H. H. Lee, *Appl. Phys. Lett.* **76**, 412 (2000).
- ¹⁵D. J. Milliron, I. G. Hill, C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **87**, 572 (2000).
- ¹⁶J. H. Choi, E. S. Lee, S. H. Choi, H. K. Baik, K. M. Song, Y. S. Lim, and S. M. Lee, *J. Vac. Sci. Technol. A* **23**, 1479 (2005).
- ¹⁷J. M. Moon, J. H. Bae, J. A. Jeong, S. W. Jeong, N. J. Park, and H. K. Kim, *Appl. Phys. Lett.* **90**, 163516 (2007).
- ¹⁸N. Koch, A. Kahn, J. Ghijsen, J.-J. Pireaux, J. Schwartz, R. L. Johnson, and A. Elschner, *Appl. Phys. Lett.* **82**, 70 (2003).
- ¹⁹A. Elschner, F. Bruder, H.-W. Heuer, F. Jonas, A. Karbach, S. Kirchmeyer, S. Thurm, and R. Wehrmann, *Synth. Met.* **111–112**, 139 (2000).
- ²⁰S. Y. Kim, K. Hong, and J. L. Lee, *Appl. Phys. Lett.* **90**, 183508 (2007).
- ²¹S. Khodabakhsh, D. Poplavskyy, S. Heutz, J. Nelson, D. D. C. Bradley, F. Murata, and T. S. Jones, *Adv. Funct. Mater.* **14**, 1205 (2004).
- ²²E. L. Hanson, J. Schwartz, B. Nickel, N. Koch, and M. F. Danisman, *J. Am. Chem. Soc.* **125**, 16074 (2003).
- ²³B. Choi, J. Rhee, and H. H. Lee, *Appl. Phys. Lett.* **79**, 2109 (2001).
- ²⁴C. Ganzorig, K.-J. Kwak, K. Yagi, and M. Fujihira, *Appl. Phys. Lett.* **79**, 272 (2001).
- ²⁵S. E. Koh, K. D. McDonald, D. H. Holt, C. S. Dulcey, J. A. Chaney, and P. E. Pehrsson, *Langmuir* **22**, 6249 (2006).
- ²⁶Q. Huang, G. A. Evmenenko, P. Dutta, P. Lee, N. R. Armstrong, and T. J. Marks, *J. Am. Chem. Soc.* **127**, 10227 (2005).
- ²⁷C. Ganzorig, M. Sakomura, K. Ueda, and M. Fujihira, *Appl. Phys. Lett.* **89**, 263501 (2006).
- ²⁸E. L. Hanson, J. Guo, N. Koch, J. Schwartz, and S. L. Bernasek, *J. Am. Chem. Soc.* **127**, 10058 (2005).
- ²⁹A. Haldi, A. Sharma, J. W. J. Potscavage, and B. Kippelen, *J. Appl. Phys.* **104**, 064503 (2008).
- ³⁰P. J. Hotchkiss, H. Li, P. B. Paramonov, S. A. Paniagua, S. C. Jones, N. R. Armstrong, J.-L. Brédas, and S. R. Marder, *Adv. Mater.* (submitted).
- ³¹M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970).
- ³²V. I. Adamovich, S. R. Cordero, P. I. Djurovich, A. Tamayo, M. E. Thompson, B. W. D'Andrade, and S. R. Forrest, *Org. Electron.* **4**, 77 (2003).
- ³³S. Yoo, B. Domercq, and B. Kippelen, *Appl. Phys. Lett.* **85**, 5427 (2004).
- ³⁴S. Naka, H. Okada, H. Onnagawa, Y. Yamaguchi, and T. Tsutsui, *Synth. Met.* **111–112**, 331 (2000).
- ³⁵T. Y. Chu and O. K. Song, *Appl. Phys. Lett.* **90**, 203512 (2007).
- ³⁶N. Koch, A. Elschner, J. P. Rabe, and R. L. Johnson, *Adv. Mater. (Weinheim, Ger.)* **17**, 330 (2005).
- ³⁷C. Tengstedt, W. Osikowicz, W. R. Salaneck, I. D. Parker, C.-H. Hsu, and M. Fahlman, *Appl. Phys. Lett.* **88**, 053502 (2006).
- ³⁸H. Fukagawa, S. Kera, T. Kataoka, S. Hosoumi, Y. Watanabe, K. Kudo, and N. Ueno, *Adv. Mater. (Weinheim, Ger.)* **19**, 665 (2007).
- ³⁹S. Braun, W. Osikowicz, Y. Wang, and W. R. Salaneck, *Org. Electron.* **8**, 14 (2007).