

Dependence of charge carrier injection on the interface energy barrier in short-channel polymeric field effect transistors

S. Alborghetti, J. M. D. Coey, and P. Stamenov

Citation: [Applied Physics Letters](#) **100**, 143301 (2012); doi: 10.1063/1.3701271

View online: <http://dx.doi.org/10.1063/1.3701271>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/100/14?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Organic \[6,6\]-phenyl-C61-butyric-acid-methyl-ester field effect transistors: Analysis of the contact properties by combined photoemission spectroscopy and electrical measurements](#)

J. Appl. Phys. **113**, 174504 (2013); 10.1063/1.4803134

[Investigation of polysilsesquioxane as a gate dielectric material for organic field-effect transistors](#)

Appl. Phys. Lett. **101**, 053311 (2012); 10.1063/1.4742891

[Reduction of charge injection barrier by 1-nm contact oxide interlayer in organic field effect transistors](#)

Appl. Phys. Lett. **100**, 013303 (2012); 10.1063/1.3673842

[Device characteristics of short-channel polymer field-effect transistors](#)

Appl. Phys. Lett. **97**, 083301 (2010); 10.1063/1.3480549

[Efficient charge injection from a high work function metal in high mobility n -type polymer field-effect transistors](#)

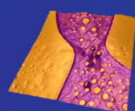
Appl. Phys. Lett. **96**, 183303 (2010); 10.1063/1.3424792

Asylum Research Atomic Force Microscopes

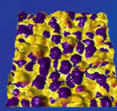
Unmatched Performance, Versatility and Support



The Business of Science®

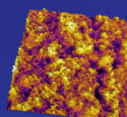


Modulus of Polymers
& Advanced Materials



Piezoelectrics
& Ferroelectrics

Coating Uniformity
& Roughness



Nanoscale Conductivity
& Permittivity Mapping



+1 (805) 696-6466
sales@AsylumResearch.com
www.AsylumResearch.com

Dependence of charge carrier injection on the interface energy barrier in short-channel polymeric field effect transistors

S. Alborghetti,^{a)} J. M. D. Coey, and P. Stamenov
CRANN and School of Physics, Trinity College, Dublin 2, Ireland

(Received 15 December 2011; accepted 18 March 2012; published online 3 April 2012)

The influence of contact materials on the electrical characteristics of field-effect transistors made from poly(3-hexylthiophene) with short-channel lengths of 80 nm is investigated. The thermally activated output current indicates the presence of a potential barrier at the electrode/organic contact. The barrier is not related to surface oxide and results in non-linear junction characteristics with activation voltage that can be only partially controlled via the work function of the contact metal. A Schottky contact at the metal/polymer interface arises from the band offset of the two materials and from interfacial dipole layers. Transistor operation with on/off ratio over 10^3 is achieved with five different electrode materials. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.3701271>]

Conjugated organic semiconductors have been the subject of intense research as potential electronic materials because they have processing advantages over conventional semiconductors, making them a competitive medium for low-cost, large-area devices. Among the most studied polymers are polythiophene derivatives, which display some of the highest hole-mobilities due to their packing in well-organized lamellae.¹ Modern devices are typically designed with a short channel length L , motivated by the need to achieve useful switching speeds and drive currents. Below a critical length, estimated as $2\ \mu\text{m}$ for polythiophene, it was observed that contact resistance can dominate the resistance of the organic channel, so that the action of a device is contact-limited.² It is, therefore, extremely important to investigate and improve charge injection.

High non-linear contact resistance is often detected in organic field-effect transistors (OFETs); it is associated with the presence of a Schottky barrier, which is induced by the difference of the work function of metal and semiconductor, and bulk transport through a depletion region in the vicinity of the interface.²⁻⁴

In this study, we investigate the influence of contact materials on the electrical characteristics of short-channel OFETs. Bottom-contact p -type OFETs with $L = 80\ \text{nm}$ were fabricated using metal electrodes with different work functions. Low-temperature studies reveal the presence of a potential barrier at the polymer-metal interface, whose origin is not simply accounted for by the difference of energy levels of the materials constituting the junction. Transistor operation is demonstrated for devices prepared with five different contacts, with a typical on/off current ratio of 10^3 ; the low-temperature field-effect mobility of poly(3-hexylthiophene) (P3HT) is also extracted.

The devices were prepared on a heavily doped n^{++} Si wafer (gate electrode) with a 210 nm thick high-quality thermal SiO_2 oxide layer (inset Fig. 1(a)). After careful cleaning of the substrates, the silicon oxide was chemically modified

with hexamethyldisilazane (HMDS) by exposure to a saturated HMDS vapor, in order to obtain a hydrophobic surface, which promotes structural ordering of the cast polymer and enhances its field-effect mobility.^{5,6} Electron beam lithography combined with a lift-off technique was then used to define interdigitated source/drain electrodes with channel length $L = 80\ \text{nm}$ and channel width $W = 900\ \mu\text{m}$, in order to maximize the channel cross-section. Electron beam evaporation was subsequently used to deposit a 2 nm thick Ti adhesion layer followed by one of the following contact materials: Co, Au, $\text{Ni}_{80}\text{Fe}_{20}$, and Al, whose work functions (Φ_M) are 5.0 eV, 5.1 eV, 5.0 eV, and 4.0 eV, respectively. Cobalt electrodes were employed as-deposited or followed by deposition of an Al_2O_3 tunnel barrier, defined by two-step oxidation of Al, which is intended to achieve a well-controlled oxide thickness.⁷ Finally, polymer films of regioregular P3HT were deposited from anhydrous-toluene solution by spin coating, in argon atmosphere, followed by annealing at $115\ ^\circ\text{C}$.⁸ The thickness of the films was found to be typically around 150 nm by AFM. The current-voltage characteristics of the transistors were acquired using a quantum design physical properties measuring system (PPMS) equipped with a 14 T magnet, making use of two cryogenic tri-axial leads for high impedance measurements, sub-femto-amp source-meters (Keithley 6430), and low bias current amplifiers. Throughout the measurements, the drain current and the gate leakage current were monitored simultaneously so that devices with negligible leakage could be selected. Measurements were performed in high-vacuum ($p < 10^{-6}$ mBar) at temperatures ranging from 300 K to 7 K.

Fig. 1(a) shows the room-temperature output characteristics of an OFET prepared with Co electrodes; the curves are linear over the range of source-drain voltages tested. Such behavior would be consistent with previous results and has typically been explained using a simple rigid-band picture, in which the similarity of the ionization potential of P3HT ($e\phi_i = 4.7\ \text{eV}$) with ($\Phi_M \sim 5\ \text{eV}$) of metals such as Co or Au leads to the absence of an interface energy barrier.^{9,10} In this case, the Fermi level in the metal is aligned with the top of the valence band in the polymer; hence, the contact is

^{a)} Author to whom correspondence should be addressed. Electronic mail: alborgs@tcd.ie. Tel.: +353 1 896 2171. Fax: +353 1 671 1759.

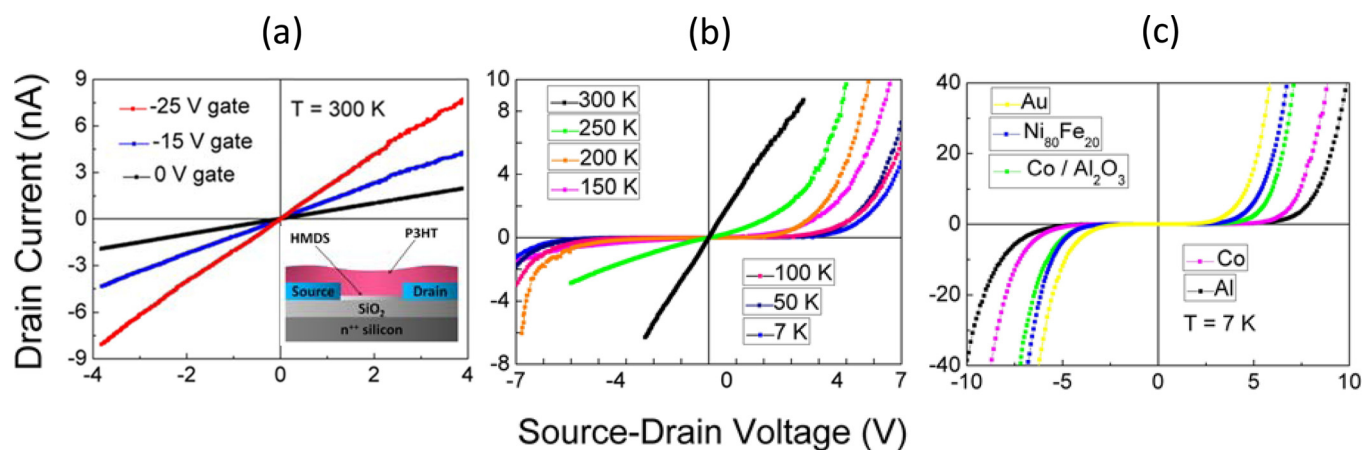


FIG. 1. (a) Room temperature output characteristics of an OFET with Co electrodes. (b) Output characteristics measured at different temperatures for the same device. (c) A comparison of the low-temperature output characteristics of OFETs with different electrode materials.

transparent for hole-injection.^{11,12} However, band offsets can be hidden by the thermal excitation of charge carriers at room temperature, and consequently, a low-temperature study is necessary to discern the real nature of contact resistance.

Fig. 1(b) shows the output characteristics at temperatures ranging from 300 K to 7 K. On lowering the temperature, the curves become pronouncedly non-linear and display clear thermally activated behavior. These results indicate that a potential barrier for hole-injection in P3HT does exist at the interface despite the nominal Fermi level alignment; carriers need to be thermally activated over the barrier before entering the semiconductor, therefore, the turn-on voltage of the junction shifts to higher bias on lowering the temperature, to compensate the reduced thermal excitation. A voltage asymmetry of the $I:V$ curves is present at all temperatures below 300 K, suggesting that the barrier heights at the source and drain contacts are slightly different. The voltage-asymmetry strongly supports the idea that the current is injection-limited, because transport in the organic medium itself should be symmetric with respect to bias, at least in the absence of in-plane magnetic field.

To gain insight into the origin of the interface energy barrier, we examined the effect of changing the contact material to Au, Ni, or Al and modifying the cobalt electrodes by introducing a thin Al_2O_3 layer between Co and P3HT. The results are summarized in Fig. 1(c), which shows the $I:V$ curves obtained with the different contacts at 7 K. Low-temperature measurements were necessary because the contact-dominated output characteristics are linear at room-temperature due to thermal excitation and do not allow for a distinction between the channel and contact resistance. The electrical characteristic of the Au-based device indicates that an energy barrier is also present at this interface, generating non-linear voltage dependence. Cobalt and gold have a similar Φ_M of 5.0 and 5.1 eV, respectively, yet a difference in the turn-on voltage of the junction is clearly observable. This could be attributed to the presence of a 2–3 nm passivation layer of CoO on the upper surface of the cobalt electrode.¹³ The effective Φ_M of the metal/oxide system differs from that of the bulk, and so transport through surface CoO appears to lead to a higher effective Schottky barrier.¹⁴ An OFET pre-

pared with Co electrodes and, in addition, 1 nm uniform barrier of Al_2O_3 display an $I:V$ curve in between those of Au and Co. Evidently, charge carriers are tunneling through the thinner surface layer so that Φ_M of Co is less affected by the presence of the oxide and resembles that of the bulk. Reinforcing this deduction, devices prepared with $\text{Ni}_{80}\text{Fe}_{20}$ ($\Phi_M = 5.0$ eV), which forms surface oxide of thickness only 0.8 nm, give a characteristic which looks like that of Co/ Al_2O_3 -based OFETs.¹⁵

Fig. 1(c) shows, amongst others, the output curve obtained with Al source-drain contacts. Al has been chosen because its Φ_M (4.0 eV) is substantially different from that of Au (5.1 eV). The turn-on voltage of the junction is considerably higher in this case, as would be expected from the larger difference with ϕ_i of P3HT, within a rigid-band picture. The Schottky barrier height appears to be controlled, at least partially, by using contact metals with different Φ_M . However, this is not the only mechanism determining the formation of an energy barrier at the interface with P3HT. The high work function of Au, in conjunction with the absence of a surface oxide, should, in principle, result in a reduced injection-barrier to P3HT. Nevertheless, a significant barrier is shown to be present in our measurements. This suggests that simple modeling, based on energy level alignment, is not fully applicable. There is a significant modification of the Fermi level in the metal, close to the interface, due to the interaction with the organic molecules. The adsorbed molecules change (compress) the metal evanescent states, eventually inducing a large interface dipole density.^{16,17} Further, a mechanism that shifts the position of the Fermi level in the polymer away from charge neutrality may also exist. It has been suggested that the region adjacent to the contact area is not composed of organic material of the same quality as the rest of the conducting channel.¹⁸ In a recent study, direct evidence of the degradation of the film morphology in the vicinity of the contacts was reported, which results in a defect-rich region at the interface.¹⁹ The physical mechanism behind the appearance of an injection barrier, in this scenario, could be a large density of localized interface-states that pins the Fermi level in the polymer, thus rendering the barrier-height independent of the ionization potential in the bulk of P3HT. The potential barrier in the semiconductor

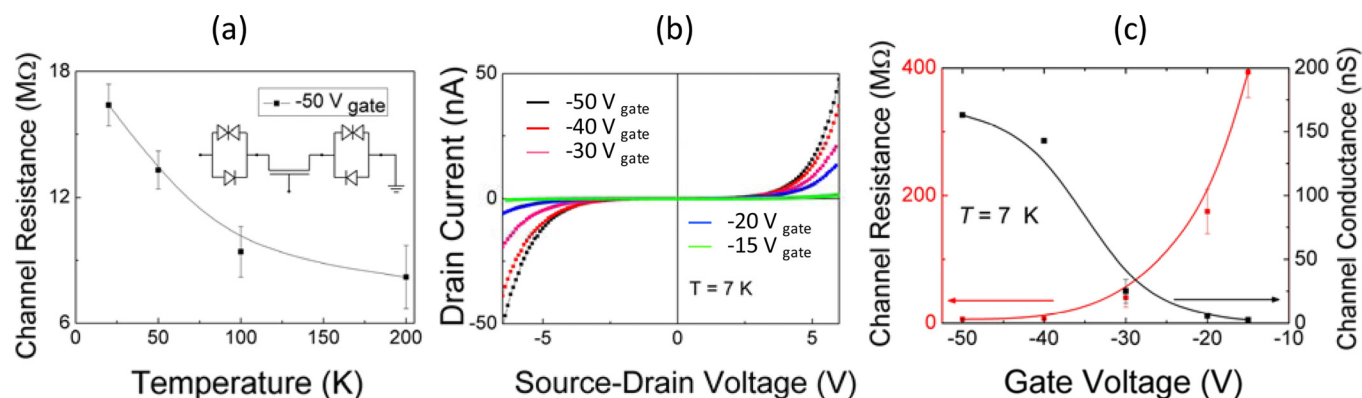


FIG. 2. (a) Channel resistance as a function of temperature. (b) Source-drain characteristics at different gate biases. (c) Channel resistance and conductance as a function of gate bias.

would, therefore, originate from the electrostatic interaction with the charge trapped at the interface. An inert layer of Al_2O_3 in the contact region prevents chemical hybridization among metal and P3HT states, but was shown not to eliminate the barrier itself, indicating that chemical dipoles do not play a dominant role. The tail of the electrons spilling out from the metal surface should significantly decay across the barrier thickness and, in turn, prevent the formation of a strong interface dipole between metal and molecular states. Instead, the height of the Schottky barrier is not greatly influenced, as visible in Fig. 1(c), where the I : V characteristic of gold devices resembles that of $\text{Co}/\text{Al}_2\text{O}_3$ devices. This supports the idea that charge trapping in polymer states contributes to the definition of the barrier height, bending the energy level in the organic side of the junction. Such a scenario explains also the voltage-asymmetry observed, by us and other groups, in the I : V curves (Fig. 1(c)), by means of small morphological differences in the polymer at the source and drain contacts, the resulting height of the Schottky barrier is different at the two electrodes.²⁰

Our measurements indicate that charge injection at the metal/polymer interface is dominated by thermionic emission at high temperature, while tunneling dominates below 100 K, where the I : V curves start to resemble each other (Fig. 1(b)). By using the equivalent circuit model of Fig. 2(a) (inset), it was possible to simulate the output characteristics and separate the contributions of the contact and the organic channel to the overall device resistance. The circuit includes the fact that injection can occur in parallel via the two aforementioned mechanisms through the contacts. Fig. 2(a) shows the plot of the extracted channel resistance at different temperatures, when a gate voltage of -50 V is applied on the $\text{Co}/\text{Al}_2\text{O}_3$ -based OFET. Notably, at this gate bias, the resistance of the organic channel changes of only a factor of two, showing that the devices are contact-limited in the range of temperature studied in this work.

Fig. 2(b) shows the output characteristics of an OFET with Au contacts at different applied gate voltages, at 7 K. No current saturation was observed in the range of biases applied, consistent with previous results in literature on contact dominated P3HT-devices.^{21,22} The resistance of the organic channel has been extracted and is plotted in Fig. 2(c), as a function of the applied gate. Saturation to a value of

about 6 MΩ is observed. The lower value, with respect to $\text{Co}/\text{Al}_2\text{O}_3$ contacts, reflects the increased number of carriers n injected by tunneling through a thinner interface barrier, recalling that no surface oxide is present on Au and $\sigma \propto n\mu$. A low-temperature field-effect mobility $\mu \approx 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is estimated, using a density of accumulated charge $n \approx 2 \times 10^{16} \text{ m}^{-2}$.²

In summary, we investigated the effect of lowering the temperature and changing contact material on the electrical characteristics of short-channel OFETs based on poly(3-hexylthiophene). The thermally activated characteristics reveal that the current is limited by field-assisted thermionic emission over an energy barrier at the metal/polymer interface. The height of the Schottky barrier can be only partially controlled via the work function of the contact metal, and two other limiting factors must also be taken into account, namely states originating in the metal and decaying in the organic and interface states originating in the organic itself. Charge trapping into the latter interface states, which are the likely consequence of a defect-rich region in the semiconductor in the vicinity of the contact (not due to contact chemical bonding), plays a significant role. Its importance was outlined by the weak effect of an artificial tunnel barrier on lowering the metal-polymer interaction. Also important is the modification of the charge neutrality level close to the interface, due to the suppression of the evanescent states originating in the metal.

The experimental results reported in this study should help to refine theoretical models explaining the mechanisms for charge injection into organic media from metallic electrodes, where all three factors determining the Schottky barrier height play comparable roles.

Despite the impediments on charge injection, on/off ratios $> 10^3$ have been obtained for all contact materials employed. The achievement of significant performance in polymeric transistors based on several different metals may prove useful in further studies, focusing on the development of new organic electronic devices.

This research was supported by Science Foundation Ireland as part of the NISE project, Contract No. 10/IN1/I3002.

¹I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, L. L. Chabinye,

- R. J. Kline, M. D. McGehee, and M. F. Toney, *Nature Mater.* **5**, 328 (2006).
- ²L. Burgi, T. J. Richards, R. H. Friend, and H. Sirringhaus, *J. Appl. Phys.* **94**, 6129 (2003).
- ³K. Seshadri and D. Frisbie, *Appl. Phys. Lett.* **78**, 993 (2001).
- ⁴N. Stutzmann, R. H. Friend, and H. Sirringhaus, *Science* **299**, 1881 (2003).
- ⁵B. S. Ong, Y. Wu, P. Liu, and S. Gardner, *J. Am. Chem. Soc.* **126**, 3378 (2004).
- ⁶L. Chua, J. Zangwill, J. Chang, E. Ou, P. Ho, H. Sirringhaus, and R. H. Friend, *Nature* **434**, 194 (2005).
- ⁷Z. G. Zhang, Z. Z. Zhang, and P. P. Freitas, *J. Appl. Phys.* **93**, 8552 (2003).
- ⁸R. D. McCullough, S. Tristram-Nagle, S. P. Williams, R. D. Lowe, and M. Jayaraman, *J. Am. Chem. Soc.* **115**, 4910 (1993).
- ⁹A. Dodabalapur, Z. Bao, A. Makhija, J. G. Laquindanum, V. R. Raju, and Y. Feng, *Appl. Phys. Lett.* **73**, 142 (1998).
- ¹⁰N. Nakanishi, K. Tada, M. Onoda, and H. Nakayama, *Appl. Phys. Lett.* **75**, 226 (1999).
- ¹¹H. Klauk, G. Schmid, W. Radlik, W. Weber, L. Zhou, C. D. Sheraw, J. A. Nichols, and T. N. Jackson, *Solid-State Electron.* **47**, 297 (2003).
- ¹²A. Salleo, T. W. Chen, A. R. Volkell, Y. Wu, P. Liu, B. S. Ong, and R. A. Street, *Phys. Rev. B* **70**, 115311 (2004).
- ¹³L. Smardz, U. Kobler, and W. Zinn, *J. Appl. Phys.* **71**, 5199 (1992).
- ¹⁴L. Giordano, F. Cinquini, and G. Pacchioni, *Phys. Rev. B* **73**, 045414 (2005).
- ¹⁵M. Salou, B. Lescop, S. Rioual, A. Lebon, J. Ben Youssef, and B. Rouvelou, *Surf. Sci.* **602**, 2901 (2008).
- ¹⁶N. Koch, A. Kahn, J. Ghijsen, J.-J. Pireaux, J. Schwartz, R. L. Johnson, and A. Elschner, *Appl. Phys. Lett.* **82**, 70 (2003).
- ¹⁷O. Tal, W. Gao, C. K. Chan, A. Kahn, and Y. Rosenwaks, *Appl. Phys. Lett.* **85**, 4148 (2004).
- ¹⁸T. Li, P. Ruden, I. H. Campbell, and D. L. Smith, *J. Appl. Phys.* **93**, 4017 (2003).
- ¹⁹K. A. Singh, T. Young, R. D. McCullough, T. Kowalewski, and L. M. Porter, *Adv. Funct. Mater.* **20**, 2216 (2010).
- ²⁰N. Koch, A. Elschner, J. Schwartz, and A. Kahn, *Appl. Phys. Lett.* **82**, 2281 (2003).
- ²¹M. D. Austin and S. Y. Chou, *Appl. Phys. Lett.* **81**, 4431 (2002).
- ²²T. Hirose, T. Nagase, T. Kobayashi, R. Ueda, A. Otomo, and H. Naito, *Appl. Phys. Lett.* **97**, 83301 (2010).