Temperature-dependent contact resistances in high-quality polymer field-effect transistors

B.H. Hamadani and D. Natelson

Department of Physics and Astronomy,
Rice University, 6100 Main St., Houston, TX 77005

(Dated: October 25, 2018)

Abstract

Contact resistances between organic semiconductors and metals can dominate the transport properties of electronic devices incorporating such materials. We report measurements of the parasitic contact resistance and the true channel resistance in bottom contact poly(3-hexylthiophene) (P3HT) field-effect transistors with channel lengths from 400 nm up to 40 µm, from room temperature down to 77 K. For fixed gate voltage, the ratio of contact to channel resistance decreases with decreasing temperature. We compare this result with a recent model for metal-organic semiconductor contacts. Mobilities corrected for this contact resistance can approach 1 cm²/Vs at room temperature and high gate voltages.

PACS numbers:
Much progress has been made in recent years in the development of field-effect transistors based on organic semiconductors (OFETs) [1]. Such devices have attracted interest for their potential applications in inexpensive and flexible electronics. Improving the device characteristics of such OFETs to have higher “on” conductances and larger on-off ratios in solution-processable materials is a technological priority.

The parasitic series resistance, $R_s$, between the organic semiconductor (OSC) and the metal electrodes is of particular interest [2]. Contacts in OFETs (extremely restricted contact geometry, essentially undoped OSCs) are distinct from those in, for example, organic light emitting diodes (large contact areas, highly doped OSCs). Contact resistance is often neglected when inferring the mobility from transistor characteristics. Different approaches have been developed to differentiate between contact and channel resistances, including analyses of single device characteristics [3, 4], scanning potentiometry [5, 6], and scaling of total resistance with channel length in a series of devices [7, 8, 9, 10]. Such experiments have already shown that $R_s$ can easily dominate $R_{ch}$ in micron-scale pentacene OFETs [7, 8], and that $R_s$ correlates inversely with mobility in polymer OFETs at room temperature [10].

The physics relevant to $R_s$ at metal-OSC interfaces is a subject of much discussion [2]. Models include Schottky contacts [4] and antiparallel Schottky diodes in parallel with a resistance [7, 8]. More sophisticated treatments include the fact that conduction in disordered OSCs is by hopping [11], image charge effects [12], and account for charge recombination at the metal-OSC interface [13]. This last model has received recent experimental support in studies that examine scaling of the contact resistivity with mobility [10, 14].

We report transport measurements in a set of OFETs made from solution cast, regioregular poly(3-hexylthiophene) (P3HT), with channel lengths from 400 nm to 40 µm. We determine the parasitic series contact resistance, $R_s$, and the true channel resistance, $R_{ch}$, from the dependence of the total source-drain resistance, $R_{on}$, on the channel length, $L$. Both $R_s$ and $R_{ch}$ increase as temperature is decreased, with $R_{ch}$ varying more rapidly. The result is that the ratio $R_s/R_{ch}$ actually decreases as $T$ is lowered; relative to the mobility, the contacts actually improve as $T$ is decreased. We compare this trend with a theoretical treatment of metal-OSC contacts, and within that model are able to estimate the Schottky barrier for hole injection from Au into P3HT. We also note that our highest quality samples have field-effect mobilities, $\mu_{FE}$, (corrected for contact effects) approaching 1 cm²/Vs, with typical values $\sim 0.2$ cm²/Vs.
Devices are made in a bottom-contact configuration (see Fig. 2 inset) on a degenerately doped $p^+$ silicon wafer used as a gate. The gate dielectric is 200 nm of thermal SiO$_2$. Source and drain electrodes are patterned using electron beam lithography. The electrodes are deposited by electron beam evaporation of 4 nm Ti and 25 nm of Au followed by liftoff. The substrates are then cleaned for one minute in a 1:1 solution of NH$_4$OH:H$_2$O$_2$ (30%), rinsed in deionized water, and exposed for one minute to an oxygen plasma.

The organic semiconductor is 98% regio-regular P3HT$^{[15]}$, a well studied material$^{[16, 17, 18]}$. As-received RR-P3HT is dissolved in chloroform at a 0.02% weight concentration, passed through PTFA 0.2 $\mu$m filters, and solution cast$^{[16]}$ onto the cleaned substrates, with the solvent allowed to evaporate in ambient conditions. The resulting film thicknesses are tens of nm as determined by atomic force microscopy (AFM). Casting produces nonuniform films, though thickness variations do not affect device performance detectably. Variations in field effect mobilities may result from subtle differences in deposition conditions. All devices are stored in vacuum dessicators until use. The measurements are performed in vacuum ($\sim 10^{-6}$ Torr) in a variable-temperature probe station using a semiconductor parameter analyzer (HP4145B). Prior to measurement, the samples are heated in the probe station to 330 K under vacuum for up to 24 hours, to remove any residual solvent and unintended doping due to exposure to atmosphere. On-off ratios at 300 K in the linear regime are typically several hundred. We report data for three arrays, each with at least eight FET devices, with parameters as described in Table I. For brevity, the data in subsequent figures are drawn from the $w = 5 \mu$m ensemble, and are representative of the other channel widths.

The devices operate as standard $p$-type FETs in accumulation mode$^{[16, 17, 18, 19, 20]}$. With the source electrode as ground, the devices are measured in the shallow channel regime ($V_D < V_G$). For each device at each gate voltage, the linear portion of $I_D - V_D$ is used to find $R_{\text{on}} \equiv \partial I_D / \partial V_D$, the total source-drain resistance. The values of $R_{\text{on}}$ are then plotted as a function of channel length for the ensemble of OFETs, as shown in Fig. 1. The slope of such a plot describes $R_{\text{ch}}$ per unit channel length. The intercept (the extrapolated resistance of a device of zero channel length) gives $R_s$, the total parasitic series resistance of the source and drain contacts. The true field-effect mobility, $\mu_{\text{FE}}$, may be inferred from the gate voltage dependence of $R_{\text{on}}$: 

$$ \frac{\partial \left[ \left( \frac{\partial R_{\text{on}}}{\partial L} \right)^{-1} \right]}{\partial V_G} = \mu_{\text{FE}}(V_G, T) w C_{\text{ox}}, $$

(1)
where $C_{ox}$ is the capacitance per unit area of the gate oxide. Mobilities inferred from the saturation regime (uncorrected for contact effects) are systematically lower than corrected $\mu_{FE}$ values, and are comparatively independent of $L$. Device $IV$ characteristics are stable with thermal cycling, and samples stored in vacuum for two months exhibit undegraded performance.

Figure 2a shows the temperature dependence of $\mu_{FE}$ for this series of 5 $\mu$m wide devices as a function of $T^{-1}$. The temperature dependence is well approximated as thermal activation, with the activation energy, $\Delta$, weakly dependent on gate voltage. For $V_G = -90$ V, $\Delta \approx 29.4$ meV; for $V_G = -30$ V, $\Delta \approx 50.8$ meV.

The temperature dependence of the parasitic contact resistance for the same devices is shown in Figure 2b. The contact resistance increases significantly as $T$ is decreased, again in an activated fashion. The activation energies are very similar to those for $\mu_{FE}$, strongly suggesting that the same physics couples both these parameters. The activation energies inferred for $R_s$ are systematically below those inferred for $\mu_{FE}$ for all gate voltages by a few meV ($\sim 4$ meV for the 5 $\mu$m ensemble of devices).

A recently developed theory of OSC-metal contacts\cite{13, 14} based on earlier work examining injection into poor conductors\cite{21} suggests why this should be so. Scott and Malliaras\cite{13} predict that the rate of injection into an OSC from a contact limited metal electrode is proportional to the OSC mobility. In particular they show

$$J_{INJ} = 4\psi^2 N_0 e\mu E \exp(-\phi_B/k_B T) \exp(f^{1/2}), \tag{2}$$

where $\psi$ is a slowly varying function of electric field, $E$; $N_0$ is the density of localized sites available for hopping conduction; $\phi_B$ is the Schottky barrier between the metal and the OSC; and the $f = e^3 E/[4\pi\epsilon\epsilon_0(k_B T)^2]$ term is due to Schottky barrier lowering. This variation of injection current density with OSC mobility has been confirmed in two-terminal OSC-metal diodes\cite{14}. In the low field limit, if the mobility itself is thermally activated with a characteristic energy $\Delta(V_G)$, one would expect $R_s \propto \exp(\Delta(V_G) + \phi_B)/k_B T$. The similarity of activation energies for $R_s$ and $\mu_{FE}$ would follow naturally, provided that the Schottky barrier between Au and P3HT is low.

Note that Eq. (2) implies that, for a given system at a fixed temperature, $R_s \propto 1/\mu_{FE}$. The constant of proportionality is temperature-dependent, and would be dominated by the Schottky barrier contribution, $\sim \exp(\Delta/k_B T)$. Figure 3 is a plot of $R_s$ vs. $\mu_{FE}$ for all three
device ensembles, including data for all gate voltages and temperatures examined. The fit demonstrates that $R_s \sim 1/\mu_{FE}^{1.09}$ over four decades of mobility. This strongly supports the mobility dependence of the injection model of Eq. (2) derived in Ref. [13], provided the Schottky barrier for the Au/P3HT interface is nearly zero. Such a small barrier is consistent with the similarity in activation energies for $R_s$ and $\mu_{FE}$ described above and seen in Fig. 2.

Fig. 4 shows the ratio of $R_s$ to $R_{ch}$ for a $L = 1 \mu m$ device from the 5 $\mu m$ wide ensemble of devices as a function of temperature. Error bars are significant because of the uncertainty in the slope and intercept parameters obtained from data like that in Fig. 1. These errors are dominated by device-to-device fluctuations within the ensemble. The ratio decreases slowly as $T$ is reduced. Within the model of Eqs. (2), this suggests that the barrier height for our Au-P3HT interface is actually slightly negative, again consistent with the systematic difference in activation energies discussed above. Relative to the channel, the contacts actually improve slightly at low temperatures, so that a device that is bulk limited at room temperature will remain so at lower temperatures.

We have used the length dependence of the channel resistance to extract the intrinsic mobility and parasitic contact resistance as a function of temperature and gate voltage for several series of bottom-contact, solution-cast polymer OFETs. The temperature and gate voltage dependence of the contact resistance and the inferred mobility support a recently developed model of charge injection from metals into disordered OSCs. We find that the ratio of contact to channel resistance actually decreases slightly as $T$ is reduced, implying a very small negative Schottky barrier for the gold-P3HT interface in these devices. Once parasitic contact resistances are taken into account, the mobility of solution-cast P3HT can approach 1 cm$^2$/Vs at room temperature, nearly an order of magnitude larger than uncorrected mobilities. These results indicate that performance of P3HT-based OFETs can be limited more by contact physics than by the intrinsic transport physics in the polymer itself.

The authors gratefully acknowledge the support of the Robert A. Welch Foundation and the Research Corporation.
FIG. 1: $R_{on}$ as a function of $L$ at 300 K for a series of P3HT OFETs with channel widths of 5 µm. Inset: $I_D$ vs. $V_D$ for several gate voltages (top to bottom, -90 V, -70 V, -50 V, -30 V, -10 V) in the $L = 2$ µm device from this series at $T = 210$ K. From -90 V to -10 V, the on-off ratio for this device is $4.1 \times 10^3$.

FIG. 2: (a) Mobility as a function of $1/T$ for several gate voltages, found via Eq. (1) in a series of 5 µm wide devices. Note the high values of $\mu_{FE}$ at large $V_G$ and high $T$. (b) Parasitic contact resistance as a function of $1/T$ for the same devices.

FIG. 3: A summary plot of contact resistivity as a function of field-effect mobility, for all three ensembles of devices, and for all gate voltages and temperatures examined. Error bars have been omitted for clarity. The fit is to a power law with exponent -1.09. Inset: $R_s(V_G) \propto R_{ch}(V_G) \times V_G(\propto 1/\mu_{FE})$ at 210 K (upper) and 100 K (lower) for the 5 µm channel width ensemble of devices. The linear dependences confirm that $R_s \sim \mu_{FE}^{-1}$, as predicted in the model of Ref. [13].

FIG. 4: $R_s/R_{ch}$ as a function of temperature for several gate voltages in the $w = 5$ µm devices, for a channel length of 1 µm. Relative to the channel, the contacts actually improve as the temperature decreases.
TABLE I: Parameters describing ensembles of devices analyzed in this study. Mobility values are obtained from $I_D - V_D$ data using Eq. (1). Contact resistivity values are computed by extrapolating $R_{on}$ back to $L = 0$. *Data for the 30 micron wide devices were at $V_G = -70$ V rather than -90 V.

| Ensemble width [µm] | min. $L$ [µm] | max. $L$ [µ] | $\mu_{FE}$ (300 K, $V_G = -90$ V) [cm²/Vs] | $R_{sw}$ (300 K, $V_G = -90$ V) [Ω-cm] |
|---------------------|----------------|--------------|------------------------------------------|-------------------------------------|
| 5                   | 0.4            | 5            | 0.73                                     | $1.1 \times 10^3$                   |
| 30*                 | 2              | 30           | 0.16                                     | $9.6 \times 10^3$                   |
| 100                 | 5              | 40           | 0.13                                     | $1.1 \times 10^4$                   |
[1] C.D. Dimitrakopoulos and D.J. Mascaro. IBM J. Res. Dev. 45, 11 (2001).
[2] J.C. Scott. J. Vac. Sci. Tech. A 21, 521 (2003).
[3] G. Horowitz, R. Hajlaoui, D. Fichou, and A. El Kassmi. J. Appl. Phys. 85, 3202 (1999).
[4] R.A. Street and A. Salleo. Appl. Phys. Lett. 81, 2887 (2002).
[5] K. Seshadri and C.D. Frisbie. Appl. Phys. Lett. 78, 993 (2001).
[6] L. Bürgi, H. Sirringhaus, and R.H. Friend. Appl. Phys. Lett. 80, 2913 (2002).
[7] H. Klauk, G. Schmid, W. Radlik, W. Weber, L. Zhou, C.D. Sheraw, J.A. Nichols, and T.N. Jackson. Sol.-State Elect. 47, 297 (2003).
[8] P.V. Nechudiov, M.S. Shur, D.J. Gundlach, and T.N. Jackson. Sol.-State Elect. 47, 259 (2003).
[9] J. Zaumseil, K.W. Baldwin, and J.A. Rogers. J. Appl. Phys. 93, 6117 (2003).
[10] E.J. Meijer, G.H. Gelinck, E. van Veenendaal, B.-H. Huisman, D.M. de Leeuw, and T.M. Klapwijk. Appl. Phys. Lett. 82, 4576 (2003).
[11] M. Abkowitz, S. Facci, and J. Rehm. J. Appl. Phys. 83, 2670 (1998).
[12] V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, and H. Bässler. J. Appl. Phys. 84, 848 (1998).
[13] J.C. Scott and G.G. Malliaras. Chem. Phys. Lett. 299, 115 (1999).
[14] Y. Shen, M.W. Klein, D.B. Jacobs, J.C. Scott, and G.G. Malliaras. Phys. Rev. Lett. 86, 3867 (2001).
[15] Sigma-Aldrich Inc., St. Louis, MO, USA.
[16] Z. Bao, A. Dodabalapur, and A.J. Lovinger. Appl. Phys. Lett. 69 4108 (1996).
[17] H. Sirringhaus, N. Tessier, and R.H. Friend. Science 280 1741 (1998).
[18] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langveld-Voss, A.J.H. Spiering, R.A.J. Janssen, E.W. Meijer, P. Herwig, and D.M. de Leeuw. Nature 401 685 (1999).
[19] A.N. Aleshin, H. Sandberg and H. Stubb. Synth. Met. 121, 1449 (2001).
[20] E.J. Meijer, C. Tanase, P.W.M. Blom, E. van Veenendaal, B.-H. Huisman, D.M. de Leeuw, and T.M. Klapwijk. Appl. Phys. Lett. 80 3838 (2002).
[21] P.R. Emtage and J.J. O'Dwyer. Phys. Rev. Lett. 16, 356 (1966).
FIG. 1: of 4, B.H. Hamadani and D. Natelson “Temperature dependent contact resistances in high quality polymer field effect transistors”, to appear in Appl. Phys. Lett.
FIG. 2: Of 4, B.H. Hamadani and D. Natelson “Temperature dependent contact resistances in high quality polymer field effect transistors”, to appear in Appl. Phys. Lett.
FIG. 3: of 4, B.H. Hamadani and D. Natelson “Temperature dependent contact resistances in high quality polymer field effect transistors”, to appear in Appl. Phys. Lett.
FIG. 4: of 4, B.H. Hamadani and D. Natelson “Temperature dependent contact resistances in high quality polymer field effect transistors”, to appear in Appl. Phys. Lett.