



Doping-dependent charge injection into regioregular poly(3-hexylthiophene)

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Abstract

We investigate charge injection from gold into regioregular poly(3-hexylthiophene) (P3HT) as a function of doping, by studying the nonlinear current–voltage characteristics of Au/P3HT/Au devices at different doping levels. The comparison of these characteristics allows us to distinguish contact-limited from bulk-limited transport. We demonstrate that there is a significant barrier to charge-injection from the contacts into the polymer, in spite of the good alignment of the Au work-function relative to the energy gap of P3HT and that the contact limitation is particularly strong at low doping levels. The contact resistance with a Ti electrode is similarly doping-level dependent. Our results show that the ability to control the doping level in organic semiconductors can be used as a tool to investigate the electronic properties of devices prepared from these materials.

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1. Introduction

The electrical behavior of semiconductors is strongly dependent on the concentration of dopants present in the material. In conventional semiconductors such as silicon, the possibility to precisely control the (local) doping level is of fundamental importance for all electronic applications. In organic semiconductors, on the contrary, such control of doping is presently out of technological reach. This poses obvious obstacles

to applications as well as to fundamental studies. For this reason, there is a need for more systematic studies of the properties of organic semiconducting materials and devices as a function of doping.

In this paper we show that even a limited control of the doping level provides information which is of use for studying the properties of organic semiconductors and devices. Specifically, we investigate charge-transport through regioregular poly(3-hexylthiophene) (P3HT) by measuring the current–voltage (I – V) characteristics of Au/P3HT/Au devices at different doping levels. Comparison of these characteristics allows us to discriminate bulk-limited from contact-limited transport. Our analysis reveals contact-limitations at the Au/P3HT interface and shows that the contact resistance increases as the doping level is decreased.

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We conclude that the Au/P3HT contacts used in our experiments are not ohmic despite the Au work function being located energetically below the P3HT HOMO level. Our conclusions have implications for P3HT-based devices, since they indicate that device performance can be further optimized by increasing the dopant concentration locally, near the contacts.

2. Materials and devices

Regioregular poly(3-hexylthiophene) is a conjugated polymer frequently employed as the semiconducting component in organic field-effect transistors [1–3]. For the study reported here, P3HT is ideally suited since its doping level can be lowered in situ, i.e., in the vacuum chamber where the electrical measurements are also performed. It has been established in literature that the *p*-doping level is related to the oxygen concentration in the polymer film [4].¹ By exposing the P3HT to air, the doping level is raised while by annealing the material in vacuum at temperatures around 425K the doping level is lowered [5].¹ Typical dopant concentrations of as-prepared films are in the 10^{17} – 10^{18} cm⁻³ range. Upon dedoping the concentration can be reduced to roughly 5×10^{15} cm⁻³ [6]. The mobility of holes in P3HT has been reported to be as high as 0.01 cm²/Vs for charge-densities in the 10^{18} – 10^{19} cm⁻³ range (field-effect transistor geometry), but several orders of magnitude lower as the charge-density is decreased ($<10^{-5}$ cm²/Vs as calculated from in-plane ohmic conductivity data [5]).

Au/P3HT/Au samples were prepared in both sandwich and surface geometries on ion-free glass substrates (Schott AF45), by spin-coating the polymer film (roughly 100 nm in thickness) in air and by vapor deposition of the Au electrodes in high vacuum (for details see Fig. 1). Electrode structures are defined by photolithography or by

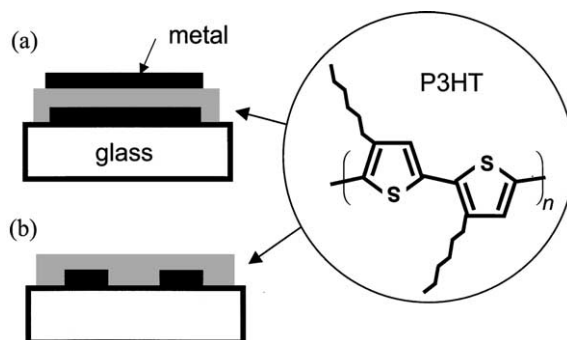


Fig. 1. Sample geometries: (a) sandwich and (b) surface. The chemical structure of the regioregular P3HT is also shown.

making use of shadow masks during vapor deposition of the Au. Measurements were done in vacuum (10^{-6} – 10^{-7} mbar). P3HT was synthesized at Philips Research Laboratories, as described elsewhere [7].

The fabrication procedure outlined above is the same as generally used to prepare diodes and transistors based on organic semiconductors. Au is normally the material of choice to contact P3HT in such devices, because the work-function of polycrystalline Au (≈ 5.1 eV) is well below the HOMO level of the P3HT (reported in literature to be 4.8 eV [8] or 4.3 eV [9]). On the basis of these numbers it can be concluded that the Fermi energy of Au is located well within the valence band of P3HT. This is often taken as the criterion for ohmic contacts—by which we mean contacts that can supply sufficient charge-carriers (holes) to enter the space-charge limited (SCL) regime [10,17]. The assumption of ohmic contacts is normally used in literature to interpret the electrical characteristics of P3HT-based devices [8,11–13]. Very recently however, a contact resistance was observed in field-effect transistor geometries with Au electrodes [14], but detailed studies of the properties of the Au/P3HT contacts are still lacking.

3. Results

Fig. 2 shows the *I*–*V* characteristics of a sandwich-type device measured after successive dedoping steps. The characteristics of the as-prepared

¹ Although the relation to the oxygen content was reported by Abdou and co-workers [4], the precise doping mechanism of P3HT has not been established yet. For example, the role of light and moisture in determining the doping level of the P3HT remains to be identified.

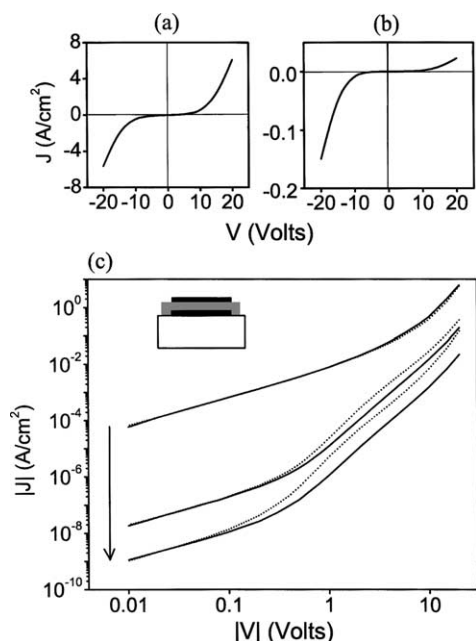


Fig. 2. Current density J versus voltage V at 300 K, for a P3HT thin film (sandwich geometry with device area $200\ \mu\text{m} \times 200\ \mu\text{m}$) as a function of doping level. The arrow points in the direction of decreasing doping levels. Decreasing doping levels were obtained by heating the device to $\approx 425\ \text{K}$ in vacuum for 30 min in between measurements. The top electrode was grounded and voltage applied to the bottom electrode. The upper panels show the data on a linear scale, as prepared (a) and after two dedoping steps (b). The lower panel (c) shows a log/log plot of the data obtained after successive dedoping steps. Full lines: positive voltages; dotted lines: negative voltages.

device are symmetric and linear (i.e., the characteristics have a slope of 1 in a log/log plot) at bias levels up to $\approx 1\ \text{V}$ and nonlinear at higher bias. With decreasing doping level, the current flowing through the device decreases by several orders of magnitude. This decrease is reversible: the characteristics return to their original value by redoping the device upon exposure to air.¹

The study of the *linear* transport regime does not easily provide information about transport through the devices, since at low voltages linear characteristics are expected both for bulk-limited [5] and contact-limited [15] charge-transport, with the current decreasing upon dedoping [5,16].

At higher bias levels we find that the current remains sensitive to the doping level up to the

highest bias investigated (Fig. 2(c)). Comparison of panels (a) and (b) in Fig. 2 furthermore reveals that upon dedoping, the electrical characteristics become strongly asymmetric. The asymmetry is such that, systematically, in all devices measured, the current flowing from top-electrode to bottom-electrode (negative voltages in Fig. 2) is larger than the current flowing in the opposite direction at opposite bias. The magnitude of the asymmetry gradually increases with progressive dedoping. For the most strongly dedoped devices the difference in current-magnitude for voltages of opposite polarity reaches one order of magnitude at room temperature. Furthermore, the current at any given bias exhibits a thermally activated behavior as a function of temperature, with a polarity-dependent activation energy.

The observation of asymmetric I - V curves in a nominally symmetric device, combined with the observation that the current in the nonlinear regime decreases substantially with dedoping, indicate that charge-transport does not occur in the SCL regime at the bias levels investigated by us, but that the nonlinear characteristics are due to contact-limitations at the P3HT/Au interfaces. Differences between top and bottom Au/P3HT interfaces result in the observation of asymmetric I - V curves despite the nominally symmetric device geometry. In a bulk-dominated device, such asymmetry should be absent. The dependence on doping level of the high-voltage I - V characteristics should also be absent in a bulk-dominated device, since in the SCL regime the amount of injected charge is by definition much larger than the amount of charge, *free or trapped*, due to dopants [17].

The difference between top and bottom contact interfaces which is at the origin of the asymmetry observed in the I - V curves can be attributed to the sequence of deposition steps used in the device preparation. On a molecular level, the polymer-on-metal interface is different from the metal-on-polymer interface and this affects the charge-injection properties. This has been reported in literature for devices based on other organic materials [18,19]. In the present case the difference is further confirmed by measurements on samples with electrodes on one side of the polymer film

(surface-type geometry). As expected, these measurements (Fig. 3) reveal the absence of asymmetry at all doping levels.²

To further demonstrate the role of contacts on the electrical characteristics of Au/P3HT/Au sandwich devices, we have investigated devices with different P3HT film thicknesses, as obtained by varying the spinning speed used to deposit the P3HT from solution, or by spinning multiple layers on top of each other [21]. Bulk-limited currents should scale with some negative power of the layer thickness. However, for dedoped P3HT with thicknesses ranging from 130 to 300 nm, no such scaling was observed.

We have also checked whether the I - V characteristics are affected by trapping of charge-carriers during the measurement sweeps. Slow trapping and release of carriers can produce hysteretical I - V curves, which might result in the appearance of asymmetry, depending on the sweep direction. However, we did not observe significant hysteresis in our experiments while sweeping the voltage from positive to negative and back again. The curves are reproduced when repeating the measurement at different sweep rates and in different sweep directions. These observations indicate that slow trapping effects do not play a role in determining the asymmetry in the I - V characteristics shown in Fig. 2.

Finally, we have compared the behavior of Au/P3HT/Au devices with that of devices in which the top electrode is made of Ti. At the Ti/P3HT interface, contrary to the Au/P3HT interface, we expect the formation of a Schottky barrier, since the work-function of the Ti (4.3 eV) does not align with the reported HOMO

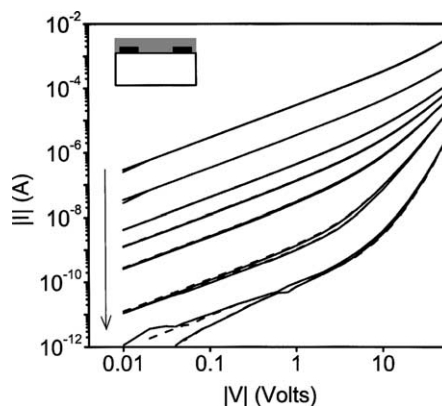


Fig. 3. Current I versus voltage V for a P3HT thin film (surface geometry with a separation between the interdigitated electrodes of 4 μm and a total electrode width 50 μm) after successive dedoping steps. After dedoping each step, I - V characteristics were measured at 300 K. The arrow points in the direction of decreasing doping levels. Positive voltage: solid lines; negative voltages: dashed lines. At all doping levels the characteristics are symmetric.

level of the P3HT. Fig. 4(a) shows the characteristics of a Ti/P3HT/Au device before and after dedoping. As expected, in both cases, a strong asymmetry is present. The asymmetry is such that injection of holes from the Ti is less efficient than from Au, in correspondence with expectations on the basis of the work-function of Ti (4.3 eV) compared to that of Au (5.1 eV). Similarly to the case of Au/P3HT/Au devices, the magnitude of the asymmetry increases with increasing dedoping, reaching three orders of magnitude. The sequence of changes in the I - V characteristics during redoping (by slowly letting air into the vacuum chamber) is shown in Fig. 4(b). First, the current limited by injection from the Ti increases while little change is observed in the other voltage polarity. Only by redoping for a longer time, the current for the other polarity starts to increase. These results provide a clear demonstration of the doping-level dependence of charge-injection from Ti into the polymer material. The similarity of these results to those obtained with Au/P3HT/Au devices seems to indicate that injection into P3HT from a metal contact is doping dependent, independent of the specific metal used.

² The observation of symmetric characteristics does not imply that charge-transport is bulk-limited in surface-geometry samples. We have found strong asymmetry in the I - V characteristics of such samples emerging after applying a constant voltage to the device for only a few minutes ("bias stressing") [20]. We attribute this to the motion of dopants under the influence of the electric field. Changing dopant concentrations near the contacts will affect the asymmetry of the I - V characteristics in a time-dependent way. As discussed elsewhere [20], this is similar to the motion of Na^+ ions in contaminated organic films.

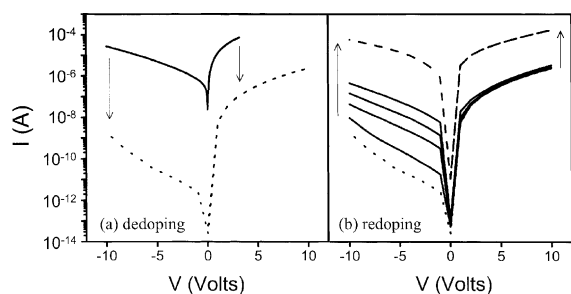


Fig. 4. Current versus voltage characteristics of a Ti/P3HT/Au device at different doping levels. Voltage V was applied to the Au (bottom) electrode, while the Ti (top) electrode was kept at ground. Panel (a) as prepared (—) and after dedoping at 440 K (···); (b) after dedoping (···), during the first few minutes of letting air into the vacuum chamber (—) and after long-time exposure to air and light (---).

4. Discussion

A doping- and temperature-dependent metal/semiconductor contact resistance with a thermally-activated dependence on temperature can be the result of different known mechanisms. The simplest example is that of thermionic emission over a Schottky barrier, with the inclusion of image charge effects [15]. The Schottky barrier height Φ in the familiar relation $I \sim \exp(-q\Phi/k_B T)$ is lowered in the presence of image-charge effects by an amount $\Delta\Phi$, given by

$$\Delta\Phi \approx \left[\frac{q^3(V - V_{bi} - kT/q)N_A}{8\pi^2\epsilon_{sc}^3\epsilon_0^3} \right]^{1/4}, \quad (1)$$

with N_A the doping level (in cm^{-3}), V_{bi} the built-in voltage, ϵ_{sc} the relative dielectric constant of the semiconductor and V the applied voltage. Lloyd et al. [13] have used this model to describe contact-limited transport in Ti/P3HT Schottky diodes at high doping levels.

In Fig. 5 we compare Eq. (1) to our measurements of the Ti/P3HT contact resistance. The figure shows the logarithm of the current plotted versus $V^{1/4}$. According to Eq. (1), $\log(I)$ should scale linearly with $V^{1/4}$ (neglecting the term $V_{bi} + k_B T/q$), with a slope depending on dopant density N_A . As can be seen in the figure, Eq. (1) seems to describe our results reasonably well at least over a

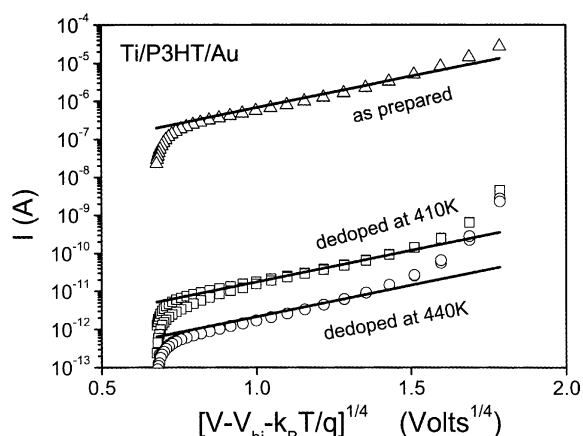


Fig. 5. Current versus $(V - V_{bi} - k_B T/q)^{1/4}$ of a Ti/P3HT/Au device. Current is injected from the Ti. Solid lines are fits to Eq. (1). $V_{bi} = 0.18$ V, as taken from [13]. From the slope of the fits we obtain (using $\epsilon_{sc} = 3$) one value of fitting parameter $N_A = 3.4 \times 10^{16} \text{ cm}^{-3}$, irrespective of the level of dedoping of the P3HT.

limited voltage scale. Also, the as-prepared device yields $N_A = 3.4 \times 10^{16} \text{ cm}^{-3}$, which is in the expected range for P3HT and. However, we find that the I - V characteristics after successive dedoping treatments all yield the same value for N_A . This indicates that Eq. (1) does not reproduce the doping dependence of the current measured experimentally and that an analysis of the contact resistance in terms of a simple Schottky barrier is not correct.

We similarly find that an analysis of the contact resistance in dedoped Au/P3HT/Au devices also fails. For these devices the value for N_A as determined from Eq. (1) ranges from 10^{17} to 10^{18} cm^{-3} . This is two orders of magnitude larger than what is expected.

These observations demonstrate that thermionic emission over a conventional Schottky barrier is not adequate to describe charge-injection into P3HT at the doping levels investigated by us. Note that by investigating one doping level only, one might conclude that the Schottky model accurately describes charge-injection from Ti into P3HT. The comparison of measurements at different doping levels, however, shows that this is not the case.

A more realistic description of charge-transport across the metal/P3HT contact should include

different phenomena. For instance, a dipole layer may form at the interface, as it has been reported for different kinds of metal/organic semiconductor interfaces [22,23]. However, in the case of the Au/P3HT interface we note that the experimentally measured temperature- and doping- dependence of the contact resistance and those of the bulk charge-carrier mobility in P3HT are very similar [5]. This suggests that transport through the interface is diffusion limited, i.e. that $I \sim \mu \exp(-q\Phi/k_B T)$ [24]. This possibility is consistent with the rather low value of μ in dedoped P3HT. A quantitative analysis of the measured transport properties on the basis of the diffusion relation is complicated and outside the scope of this paper. Here we only point out, on the basis of our measurements, that the ability to control the doping level at the contact gives one an additional experimental handle to investigate interfacial properties.

5. Conclusions

In conclusion we have shown that even a limited control of the doping level in organic materials gives useful information about bulk- or contact-limitations of charge-transport. In the present case, tuning the doping concentration in P3HT by annealing thin films in vacuum or exposing them to air, has allowed us determine that bulk-dominated transport in the SCL regime is not responsible for the nonlinearities observed in the I - V curves of Au/P3HT/Au thin-film devices. Instead, they are due to contact effects. The presence of a large, doping-level dependent contact resistance at the P3HT/Au interface provides clear experimental evidence that a good alignment of the work-function in Au with respect to the HOMO level of P3HT is not sufficient for the fabrication of ohmic contacts. The contact resistance of the Ti/P3HT interface is similarly sensitive to doping level. We suggest that the doping-level dependent contact effects are due to the low mobility of charge-carriers in the organic material directly adjacent to the contact interface and the resulting diffusive motion of holes crossing the interface. Our results are relevant for applications, since the presence

of a contact resistance is a limiting factor for device performance. We expect that the study of transport as a function of doping level can provide useful information about a range of organic semiconductors and devices based on these materials.

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