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# Enhancement of the hole injection into regioregular poly(3-hexylthiophene) by molecular doping

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The hole injection in Schottky barriers formed between *p*-type doped regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) and silver (Ag) is investigated. The rr-P3HT is controllably doped using the acceptor 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). We demonstrate that only one order of magnitude increase in the background hole density  $p_0$ , from  $2 \times 10^{16}$  to  $2 \times 10^{17}$  cm<sup>-3</sup>, enhances the hole injection with two orders of magnitude. The hole injection barrier is lowered by 0.5 eV and exhibits a linear dependence on  $p_0$ , which can be explained by doping induced surface charges. © 2010 American Institute of Physics. [doi:10.1063/1.3464560]

Charge injection is an important process with regard to the performance of current-driven organic devices as organic light-emitting diodes and organic field-effect transistors (OFETs). Presence of charges at organic/metal interfaces can effectively lower the charge injection barrier by the formation of dipoles.<sup>1</sup> For regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) it has been found that the band alignment at the contact can be drastically altered using a doping/dedoping process by exposing rr-P3HT films to air and vacuum, respectively.<sup>2</sup> Furthermore, by using iodine as dopant the conduction in rr-P3HT films could be enhanced, and within specific doping regimes the dependence of the conductivity on temperature has been investigated.<sup>3</sup> However, for organic semiconducting devices molecular doping is preferable, since field-induced drift of the relative large-size charged molecular dopants can be suppressed. Recently, rr-P3HT based OFETs doped with the strong acceptor 3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) have been reported.<sup>4</sup> Upon doping the field effect mobility increased by a factor of 30 and the threshold voltage was controllable by adjustment of the doping concentration.

In conventional semiconductors an increased doping level leads to an enhancement of the electric field at the metal/semiconductor interface. The increase in the electric field then gives rise to a reduction in the injection barrier due to image force lowering. At very high doping densities, typically in the  $10^{19}$  cm<sup>-3</sup> regime, the band bending becomes sufficiently strong that charge carriers can directly tunnel into the semiconductor, leading to the formation of an Ohmic contact. In this paper, we investigate the effect of *p*-type doping on the injection efficiency of holes into rr-P3HT from a nonOhmic Ag contact. Surprisingly, already at relatively low free hole densities  $p_0$  of only  $10^{17}$  cm<sup>-3</sup> the Ag contact with an injection barrier of  $\sim 0.6$  eV becomes nearly Ohmic. The image force lowering at this doping density only amounts to 0.1 eV and can therefore not explain the strong enhancement of the hole injection of two orders of magnitude. The strong decrease in the injection barrier together

with its linear dependence on  $p_0$  is explained by the formation of a F4-TCNQ surface layer.

To study the dependence of the hole injection upon doping Schottky diodes were fabricated in which the undoped and doped rr-P3HT layers were sandwiched in between a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) bottom electrode and a Ag top contact. The PEDOT:PSS, forming an Ohmic hole contact with P3HT, was spun on precleaned ITO/glass substrates, followed by an annealing step at 140 °C for 10 min to remove residual water. The rr-P3HT was purchased from Rieke<sup>®</sup> Metal and F4-TCNQ was obtained from Sigma-Aldrich and used without further purification. The P3HT host and F4-TCNQ dopant were separately dissolved in chloroform. After being filtered with a 0.2 μm pore-size filter they were blended and stirred on a hotplate of 50 °C for approximately 1 h. The blends were then spin coated in a nitrogen-purged glove box. Addition of 20~30 μL of dimethylsulfoxide to the rr-P3HT solution helped to prevent aggregation of the dopants, yielding smooth films.<sup>5</sup> Finally, a 80 nm Ag top electrode was deposited on the polymer by thermal evaporation at a chamber pressure of  $10^{-7}$  mbar. The electrical characterization of the diodes was performed in nitrogen environment using a Keithley 2400 SourceMeter.

Figure 1 represents the *J*-*V* characteristics of rr-P3HT Schottky diodes for various doping levels with a molar ratio of 1:300, 1:100 and 1:50, respectively. Due to relatively large energy offset between the Fermi level of Ag ( $\sim 4.3$  eV) and the highest occupied molecular orbital (HOMO) of rr-P3HT ( $\sim 4.9$  eV), a hole blocking contact is formed leading to an injection limited current (ILC) in reverse bias. An important question is now how many of the dopants are ionized and contribute to a doping induced free hole density  $p_0$ . In a recent paper<sup>5</sup> we demonstrated that controlled *p*-type doping with F4-TCNQ can be achieved in solution processed poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) using F4-TCNQ as a dopant. By using a co-solvent aggregation can be prevented and doped films can be deposited. While the undoped MEH-PPV exhibited space-charge limited currents (SCLC) the addition of doping resulted in a clear Ohmic behavior at low bias.

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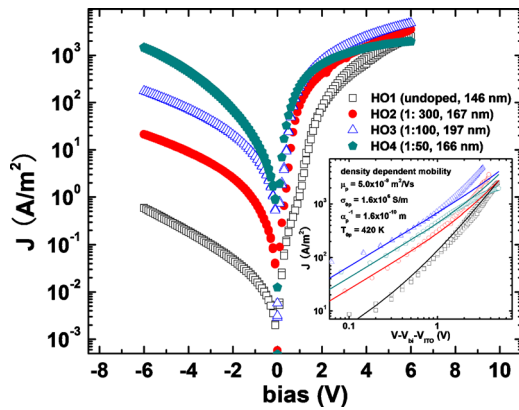


FIG. 1. (Color online) Current–voltage characteristics of Ag/rr-P3HT Schottky diodes as a function of doping concentration. The inset shows the experimental and numerically calculated  $J$ – $V$  characteristics using a density-dependent mobility model.

From this low bias regime the free hole concentration due to doping can be derived, under the condition that the density dependence of the hole mobility is taken into account.<sup>5</sup> Furthermore, the free hole densities can be determined from impedance measurements on Schottky diodes.

In order to analyze the forward bias  $J$ – $V$  characteristics we use a density-dependent hole mobility of Eq. (1) (Ref. 6) which was derived from an exponential density-of-states (DOS) and later on was expanded with an inclusion of the field-dependence<sup>7</sup> or the corresponding expression from a Gaussian DOS<sup>8,9</sup>

$$\mu_h(p, T) = \mu_h(0, T) + \frac{\sigma_0}{e} \left[ \frac{\left(\frac{T_0}{T}\right)^4 \sin\left(\frac{\pi T}{T_0}\right)}{(2\alpha)^3 B_C} \right]^{T_0/T} p^{T_0/T-1} \quad (1)$$

with  $\mu_h(0, T) = 5.0 \times 10^{-9} \text{ m}^2/\text{V s}$  representing the hole mobility at low densities,  $\sigma_0 = 1.6 \times 10^6 \text{ S/m}$  being the prefactor for the conductivity,  $\alpha^{-1} = 1.6 \times 10^{-10} \text{ m}$  as effective overlap parameter between localized states,  $T_0 = 420 \text{ K}$  as a measure of the width of the exponential density of states, and with  $B_C = 2.8$  being the critical number for the onset of percolation.<sup>6</sup> The simulated  $J$ – $V$  characteristics (lines) are shown in the inset of Fig. 1 together with the measurements (symbols). In order to confirm the values of  $p_0$  as a function of doping level also the depletion capacitance  $C_p$  was measured on the same devices using impedance spectroscopy. The resulting dependence of  $C_p$  on the applied voltage, characterized by  $C_p^{-2} - V$ , is plotted in Fig. 2. The linear response as measured on the doped devices confirms the formation of a depletion region that is narrower than the thickness of the rr-P3HT layer. By using the Schottky-Mott relation, given by  $N_d = 2/[q\epsilon_0\epsilon_r(dC_p^{-2}/dV)]$ , where  $N_d$  is the amount of ionized dopants ( $=p_0$  in our case),  $\epsilon_0\epsilon_r$  the permittivity of rr-P3HT, and  $dC_p^{-2}/dV$  the slope of the plot in Fig. 2,  $p_0$  has been calculated and plotted as a function of doping concentration in the inset of Fig. 2. As earlier observed for MEH-PPV also in P3HT the amount of free holes  $p_0$  depends linearly on the doping concentration. Furthermore, the  $p_0$  values obtained from the impedance spectroscopy are in good agreement with the hole densities found from the analysis of the  $J$ – $V$  characteristics.

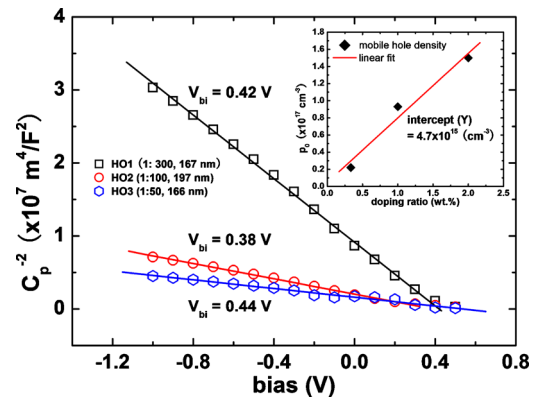


FIG. 2. (Color online) Schottky-Mott plot of the depletion capacitance measured on Ag/F4-TCNQ doped rr-P3HT diodes. The inset shows the mobile hole densities  $p_0$ , calculated from the slope of  $C_p^{-2} - V$ , as a function of the dopant concentration.

As a next step we investigate the injection limited hole currents from the Ag into P3HT in reverse bias. At low doping level this ILC is clearly much lower than the SCLC in forward bias. For the undoped P3HT the rectification ratio is on the order of  $10^5$ . However, for a molar doping ratio of 1:50, corresponding to a free hole density  $p_0$  of  $1.5 \times 10^{17} \text{ cm}^{-3}$  the ILC becomes nearly Ohmic since the  $J$ – $V$  curve becomes almost symmetric. In the classical diffusion-limited injection model for low mobility semiconductors, given by  $J = qN_V\mu_p(T, p)E \exp(-\phi_B - \Delta\phi/kT)$  with  $N_V$  the effective density of states, the increase in the ILC with the electric field  $E$  is governed by the barrier lowering  $\Delta\phi_B$  due to the image potential, given by  $\Delta\phi = \sqrt{qE_m/4\pi\epsilon_0\epsilon_r}$ . The resulting barrier lowering then depends on the electric field at the metal/semiconductor interface  $E_m = \sqrt{2qN_D/\epsilon_0\epsilon_r(V_{bi} - V - k_B T/q)}$ , which is also dependent on the doping density  $N_D$ . To explain the strong enhancement of the ILC upon doping we first calculate the energy band diagram as a function of distance  $x$  from the Ag contact within the depletion region of the Schottky diodes using the experimentally determined  $p_0$ , as shown in Fig. 3. The reduced width of the depletion region at higher doping originates from the stronger band bending due to a higher density of ionized dopants. For the free carrier densities  $p_0$  of  $2 \times 10^{16} \text{ cm}^{-3}$  (1:300),  $9 \times 10^{16} \text{ cm}^{-3}$  (1:100) and  $1.5 \times 10^{17} \text{ cm}^{-3}$  (1:50) the resulting barrier lowering  $\Delta\phi_B$  amounts to 70 meV, 99 meV and 118 meV, respectively. These relatively small values of  $\Delta\phi_B$  are insufficient to ex-

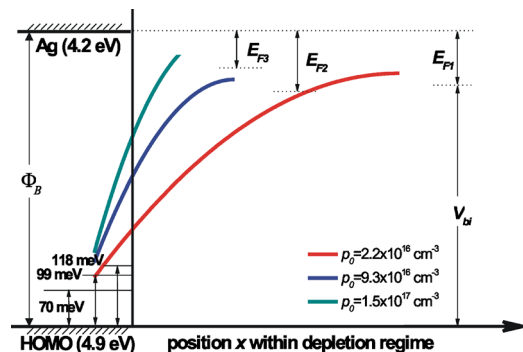


FIG. 3. (Color online) Calculated energy band diagram in the depletion region as a function of the distance  $x$  from the Ag contact, using the experimentally obtained  $p_0$ . The image potential is also taken into account.

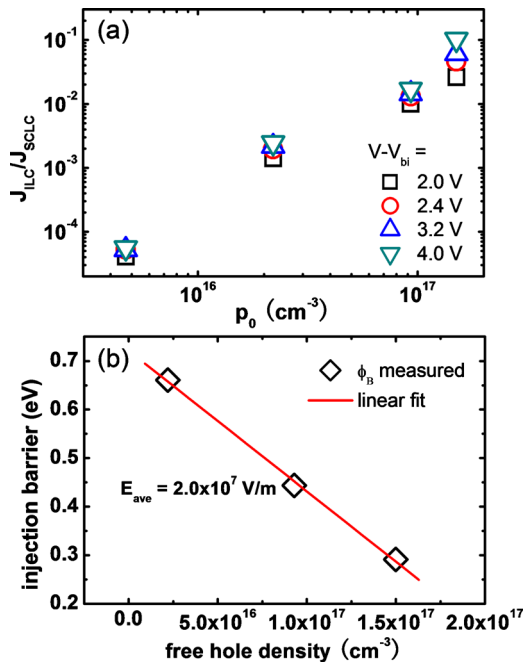


FIG. 4. (Color online) (a) Ratio of the ILC to the bulk limited SCLC as a function of the background hole density at various applied bias. The built-in voltages have been subtracted to eliminate the effect of the diffusion current at low electric field. (b) Injection barriers calculated from the rectification ratios of the  $J$ - $V$  characteristics as a function of the mobile carrier density.

plain the occurrence of a nearly Ohmic contact for a  $p_0$  of only  $1.5 \times 10^{17} \text{ cm}^{-3}$ . In order to break down the Ag/P3HT injection barrier of 0.6–0.7 eV our simulations indicate that  $p_0$  should be at least on the order of  $\sim 10^{19} \text{ cm}^{-3}$ . Therefore, for the moderate doping levels in our solution processed P3HT another mechanism should be responsible for the strong enhancement of the ILC.

Upon increased doping level also the Fermi level in the P3HT will move closer to the HOMO level, leading to a decrease in the injection barrier. Assuming that the DOS is Gaussian, with a total number of sites of  $2 \times 10^{20} \text{ cm}^{-3}$  and a half-width of 94 meV,<sup>6,10</sup> we can calculate the position of the Fermi level for the different doping levels. For dopant densities of  $2 \times 10^{16} \text{ cm}^{-3}$ ,  $9 \times 10^{16} \text{ cm}^{-3}$ , and  $1.5 \times 10^{17} \text{ cm}^{-3}$ , the Fermi-level is 0.4 eV, 0.36 eV and 0.34 eV away from the middle of the Gaussian DOS, respectively. Thus the variation in the Fermi level with doping can only account for a barrier reduction in 60 meV, and is also therefore not responsible for the efficient injection at  $p_0 = 1.5 \times 10^{17} \text{ cm}^{-3}$ .

The interpretation of the measurements are complicated by the fact that until now for conjugated polymers there are no models available that quantitatively describe the observed dependence of the ILCs on the injection barrier height. For a series of polymers and electrodes we recently found that the current is reduced by one order of magnitude when the injection barrier is increased by 0.25 eV.<sup>11</sup> As a result a 1.0 eV injection barrier leads to an ILC that is four orders of magnitude lower than the bulk-limited SCLC. Figure 4(a) shows the rectification ratios of the measured  $J$ - $V$  characteristics as function of the free hole density  $p_0$  under various bias. Using the empirical 0.25 eV/decade in Fig. 4(b) the barrier height  $\Phi_B$  is plotted as a function of  $p_0$ . The  $\Phi_B$  corresponding to the undoped device is slightly larger than the value expected

from the known energy offset between the Fermi level of Ag (4.3 eV) and HOMO of rr-P3HT (4.9–5.0 eV). This deviation can be attributed to the fact that the work function of Ag varies with the evaporation conditions. From Fig. 4(b) it is evident that  $\Phi_B$  linearly decreases with increasing  $p_0$ . This is in contrast with the classical Schottky barrier, where  $\Delta\phi \propto N_d^{1/4}$ . For OLEDs based on evaporated small molecules Ohmic contacts could be formed at high doping levels ( $10^{19} \text{ cm}^{-3}$ ) of F4-TCNQ. Then tunneling through the very narrow space-charge region starts to dominate the injection, leading to Ohmic contacts.<sup>12–14</sup> However, it has been observed by Koch *et al.*<sup>15</sup> that the adsorption of F4-TCNQ on Au leads to a reduction in the hole-injection barrier of as much as 1.2 eV. Furthermore, it was shown that the reduction in the injection barrier was linearly dependent on the amount of adsorbed molecules at noncomplete surface coverage. In our experiment we deposit a blend of P3HT and F4-TCNQ, which is different than co-evaporation F4-TCNQ with an organic host. Since F4-TCNQ is better soluble in chloroform than P3HT it is expected to phase separate and to migrate to the surface where it will form a dipole due to electron transfer. The reduction in the barrier will then also linearly depend on the amount of molecules on the surface. This mechanism explains the strong decrease in the injection barrier at relatively low doping levels as well as its linear decrease with increasing doping density. An important consequence is that for devices based on solution processed conjugated polymers only very low doping concentrations are required to form Ohmic contacts.

In conclusion, we have studied the effect of molecular doping on the charge injection in rr-P3HT based Schottky diodes. A strong increase in the ILC is observed for already moderate doping levels of  $10^{17} \text{ cm}^{-3}$ , that cannot be attributed to barrier lowering due to image forces. The linear reduction in the injection barrier height upon doping can be explained by the presence of a F4-TCNQ surface layer.

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