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Schottky contacts on a highly doped organic semiconductor

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Schottky-diode action in thiophene oligomer is investigated by current-density–voltage (J-V) and capacitance-voltage (C-V) measurements. An energy-band diagram is deduced that explains the diode characteristics for both unintentionally and highly doped thiophene oligomers. We conclude that the diode consists of a thin layer of low ionizable acceptor density (p^-) at the metal-oligomer interface and a semiconductor bulk layer that has a higher dopant concentration (p^+). The presence of the lower doped p^- layer leads to a built-in voltage of 0.5 V, which is both experimentally observed and predicted using standard Schottky theory. Differences in J-V characteristics upon doping the thiophene semiconductor are explained by the Schottky-barrier lowering effect for the reverse current density, and by a higher conductivity of the bulk for the forward current density.

The availability of organic semiconductors with an acceptable level of stability and processability has stimulated their use as active components in electronic devices. Semiconducting organic oligomers and polymers are of particular interest, since they possess advantageous mechanical and processing properties for the design and fabrication of various classes of semiconducting devices.

Thin film diodes have been made from various p-type unintentionally doped organic semiconductors, that were sandwiched between a low work function metal (e.g., Al, In, Ag, Mg) and an Ohmic contact (e.g., Au).[1–7] These diodes exhibit rectification ratios varying from $10–10^6$ and diode quality factors of 1.2–4. The forward current density (J_F) at 1 V forward bias [J_F(1 V)] is always small ($\sim 10^{-4}$ A cm^{-2}) due to the large bulk resistivity. Since these diodes are majority carrier devices, their switching speed is determined by the RC time constant which is the product of the depletion layer capacitance and the diode series resistance. Due to the large bulk series resistance, the switching speed of these diodes is slow (typically <100 Hz).

Doping of the oligomer is required to decrease the bulk resistivity of the diode, and, hence, to increase the switching speed. However, highly doped oligomers in Schottky diodes are expected to form only thin barriers, if any. For example, for a one-sided abrupt junction we have for the depletion width w,[8]

$$w = \sqrt{2\epsilon_0 \epsilon_r V_R / qN_A}, \tag{1}$$

where ϵ_0 and ϵ_r (≈ 2) are the absolute and relative dielectric constants, respectively. For a typical reverse voltage V_R across the junction of 1 V, one finds, for ionizable acceptor densities N_A of $10^{20}-10^{21}$ cm^{-3}, a depletion width of about 10 Å. For such a thin depletion layer one expects the current transport to be dominated by tunneling processes, resulting in an Ohmic and a nonrectifying contact behavior.[9] Nevertheless, we have made Schottky-type diodes from highly doped oligomers, with considerably improved J_F(1 V) up to a few A cm^{-2}, and with rectifications of four orders of magnitude.[10] It was found that in these devices, J_F(1 V) is not limited by the resistivity of the bulk but by a poorly conducting layer close to the metal-oligomer interface, previously referred to as an "insulating" layer.[10] Similar diodes have been reported by Kuo *et al.*[11]

In this paper we give a detailed energy-band diagram description of our diodes from which we conclude that they are best described as conventional Schottky diodes and not as metal insulator semiconductor (MIS) devices.[10,11] We present the result of current-density–voltage (J-V) and capacitance-voltage (C-V) measurements on both unintentionally and highly doped thiophene oligomer diodes. We find that both types of diodes exhibit a gradient in the ionizable acceptor density N_A, which separates a partially undoped *semiconducting* p^- layer at the metal-oligomer interface from the bulk semiconductor, which has at least an order of magnitude higher (p^+) acceptor density. It is this p^- layer, which has a low, almost insulatorlike, conductivity, that limits J_F(1 V) in these devices. From the dopant profile we have calculated energy-band diagrams that are consistent with the obtained J-V and C-V data. These enable a detailed understanding of the electrical behavior of these diodes.

The organic semiconductor we use is α,α'-coupled dodecathiophene oligomer, substituted with four n-dodecyl side chains at the thiophene rings 2, 5, 8, and 11: $T_{12}d_4$ (Syncom B.V, University of Groningen).[12] $T_{12}d_4$ is doped with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Janssen Chimica, 98%) in the THF solution (Merck, pa).[10] The doping level is defined as the percentage of donated holes per thiophene ring. (Note that one DDQ molecule can donate two holes so that the number of DDQ molecules is half that of the doping level.) We studied two types of diodes made from $T_{12}d_4$ solutions to which either DDQ is added to a doping level of 5% (5% doped diodes) or no DDQ is added (unintentionally doped diodes). A doping level of 5% corresponds to a donated hole density of about 4×10^{20} cm^{-3}. Films are spin-coated (typical thickness: 4000 Å) on glass substrates previously covered with four evaporated Au stripes for a determination of the bulk conductivity σ_{bulk}. Au is an Ohmic contact to (doped) $T_{12}d_4$. For the diode we use as bottom electrode Au, while for the top Schottky contact In is evaporated onto the film at a pressure of about 10^{-6} Torr. The setup for measuring the J-V and C-V data is described

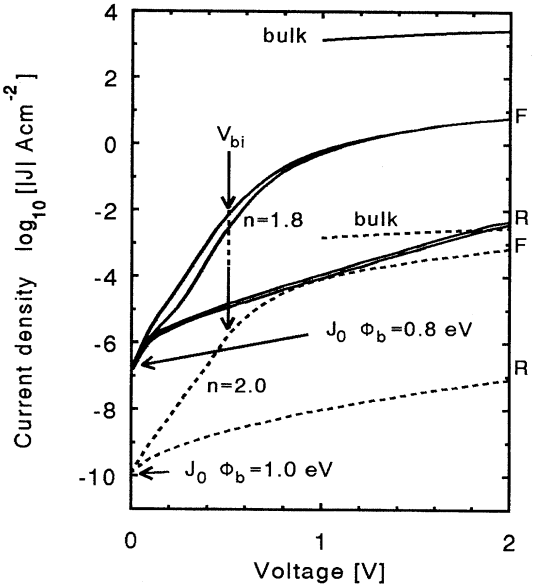

FIG. 1. Current-density–voltage characteristics of 7000 Å thick film diodes evaporated with 2000 Å thick In contacts. (—) 5% doped (σ_{bulk}=0.1 S/cm) and (- - -) unintentionally doped ($\sigma_{bulk}=10^{-7}$ S/cm). The forward and reverse current density traces of both diodes are indicated by F and R, respectively. J_F increases exponentionally with voltage, up to about the built-in voltage V_{bi} of the diode, as indicated by arrows. Interpolating this part of J_F towards zero voltage, gives the saturation current density J_0. The short lines between 1 and 2 V indicate the level at which the forward current density would have been in the case that it was limited by only the conductivity of the bulk of the semiconductor σ_{bulk}. The difference is due to the resistance of the p^- layer.

in Ref. 10. All measurements were taken at ambient temperature (300 K) and atmosphere.[8]

Figure 1 shows the current density versus voltage characteristics of two diodes, one unintentionally doped and the other 5% doped. We model the J-V curves using conventional thermionic-emission theory:

$$J=J_0\left[\exp\left(\frac{qV_b}{nk_BT}\right)-1\right], \tag{2a}$$

$$J_0=A^*T^2\exp\left(\frac{-q\phi_b}{k_BT}\right), \tag{2b}$$

where A^* is the Richardson constant, q (>0) the elementary charge, k_B the Boltzmann constant, T the temperature, and V_b the bias voltage across the diode. Both curves show four orders of magnitude of rectification, while the saturation current density J_0, found by interpolation of the steep exponential slope of the J_F trace towards J at $V_b=0$ V, is shifted by three orders of magnitude upon doping. These values of J_0 imply [cf. Eq. (2b)] that the Schottky barrier ϕ_b changes from about 1.0 to 0.8 eV upon doping. Note that barriers obtained from J-V data do not necessary give the *full* height Schottky barrier ϕ_{b0} since they do not include, for example, barrier lowering effects. The *full* Schottky-barrier height is the the barrier height at zero electrical field F at the metal-oligomer interface and is determined by the difference in

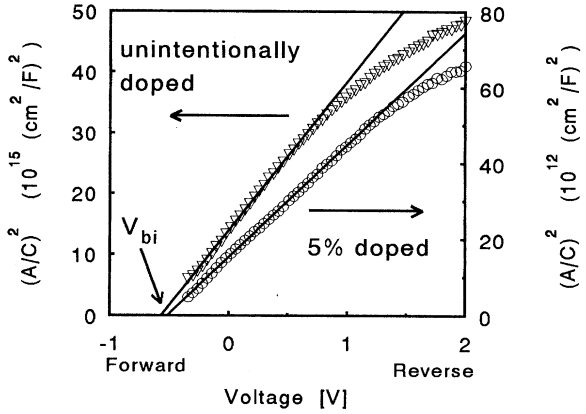

FIG. 2. This plot shows the (area/capacitance)^2 versus the bias voltage of both the same unintentionally and 5% doped diodes of Fig. 1, measured at 10 and 1000 Hz, respectively. Interpolating the straight part of the curves towards the voltage axis gives the built-in voltages V_{bi} of the diodes: 0.57 and 0.51 V for the unintentionally and the 5% doped diodes, respectively.

electron affinity between the metal and the semiconductor. Therefore, it does, of course, not vary upon doping. From the exponential slope between 0 and 0.5 V forward bias in Fig. 1, the quality factor n is found to be 2.0 and 1.8 for the unintentionally and 5% doped sample, respectively. The voltage at which the exponential part of the forward trace bends over (indicated by arrows in Fig. 1) gives an indication of the built-in voltage (V_{bi}) of the diode. For both curves V_{bi} is about the same, 0.5–0.6 V. At high forward bias, beyond 1 V, the current density depends superlinearly on the forward voltage V_F: Approximately $J\propto V_F^{2.5}$. This is indicative of electrical transport that is dominated by space charge limited current (SCLC).[13] In this voltage regime, J_F is significantly smaller than what is anticipated on the basis of σ_{bulk}. The *bulk limited* forward current density level is indicated by the lines between 1 and 2 V in Fig. 1.

For both the unintentionally and the 5% doped diodes we have measured the C-V dependence at 10 and 1000 Hz, respectively. With increasing reverse bias the capacitance is found to decrease due to the increasing depletion width of the diode. Figure 2 shows the (area/capacitance)^2 versus voltage, where from the linear interpolation of the data at low voltages, almost similar values for V_{bi} are found: 0.57 and 0.51 V for the unintentionally and 5% doped diodes, respectively.[10] These values are in good agreement with the built-in voltages deduced from the J-V curves (see Fig. 1, about 0.5–0.6 V). At higher reverse voltages the curves deviate from linear behavior and start to saturate, which is typical for diodes with nonflat dopant profiles.

Using the C-V data we have determined the depth dependence of the ionizable acceptor density N_A as a function of w, as shown for both diodes in the bottom part of Figs. 3(a) and 3(b).[8] Both diodes have close to the Schottky metal interface a constant level of low acceptor density at 2.7×10^{15} and 2.5×10^{18} cm^{-3}, respectively, which we identify as the partially undoped p^- layer. Deeper into the film, the onset of a gradient towards a much larger acceptor density that is present in the bulk of the semiconductor film is observed, which we indicate as the p^+ layer. This onset starts

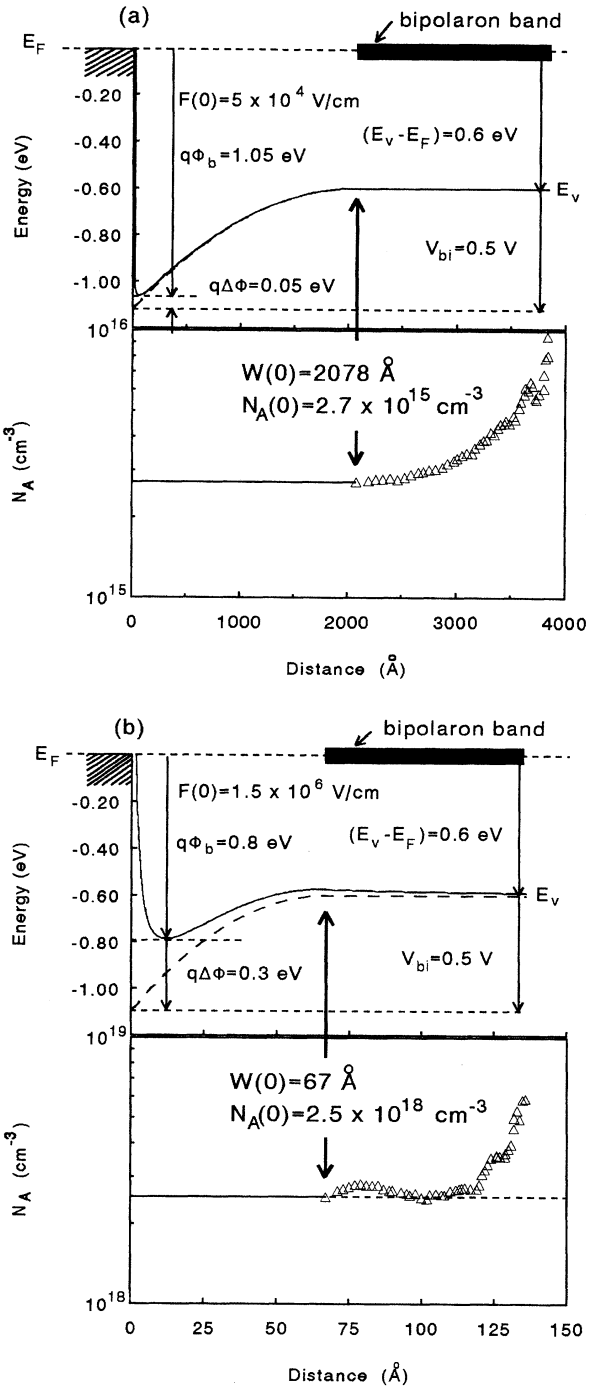

FIG. 3. The bottom parts show the profile of the ionizable acceptor density as a function of the depletion depth of the diode, measured from the In-metal-oligomer interface as deduced from the data shown in Fig. 2: (a) unintentionally doped and (b) 5% doped diodes. In the top parts the corresponding band bending of the valence band is displayed (dashed line) assuming a constant acceptor density up to the metal interface. The solid line is the final energy band after including the effect of the image force which causes the lowering of the barrier. The large arrows indicate the depletion depth at zero voltage $w(0)$ and its acceptor density. The first bipolaron band is tentatively positioned at the Fermi level and is absent in the depletion region of the diode.

for the unintentionally doped diode at about 2000 Å and for the doped diode at about 120 Å. Through doping, N_A in both the p^- and p^+ layers is increased. The low acceptor density in the p^- layer makes this layer in both diodes highly resistive ($\sigma<10^{-7}$ S/cm). Therefore, it is this low doped p^- layer that limits the forward current density in both diodes. For the p^+ layer, we note that between the unintentionally and the 5% doped $T_{12}d_4$, only one order of magnitude lower bulk dopant density is needed, to obtain the observed six orders of magnitude difference in σ_{bulk} (cf. Fig. 1).[10,12] This results in an upper limit estimate of 4×10^{19} cm^{-3} for the bulk dopant density of unintentionally doped $T_{12}d_4$.

In the top part of Figs. 3(a) and 3(b), we show the band bending $V(x)$ of the valence band, which has been calculated by solving the Poisson equation:

$$\frac{-\delta^2V(x)}{\delta x^2}=\frac{\delta F(x)}{\delta x}=\frac{\rho(x)}{\epsilon_s}=\frac{qN_A(x)}{\epsilon_s}, \tag{3}$$

with x the distance from the metal, F electric field, ρ charge density, and $\epsilon_s=\epsilon_0\epsilon_r$ as in Eq. (1). For the doping profile $N_A(x)$ we use the measured values where applicable and assume a constant acceptor density from the metal interface down to the first experimental data point. Using appropriate boundary conditions $[V(0)=-\phi_{b0}, V(w)=-\phi_{b0}+V_{\text{bi}}$, and $F(w)=0]$ we calculate a band bending of $V_{\text{bi}}\approx0.5$ V (Fig. 2 dashed curve), which is in good agreement with the values found by analyzing the C-V and J-V data of Figs. 1 and 2. These consistent results do not support a MIS description of the diodes, because the rectification occurs at the metal p^- interface and because insulators do not contain such high ionizable acceptor densities. Furthermore, at forward bias, the C-V data do not yield a frequency and bias independent capacitance which would have been indicative for the presence of an insulating layer. Therefore, our diodes should be considered as Schottky diodes.

From solving Eq. (3) one also obtains the electric field at the metal interface: $F(0)=5\times10^4$ and 1.5×10^6 V/cm for, respectively, the unintentionally and 5% doped diodes. This latter field is sufficiently large to cause barrier lowering of ϕ_{b0} by an amount $\Delta\phi$, through the image force effect.[8] In the energy-band diagrams of Fig. 3 this is modeled by adding the potential energy of the image force V_{IF},

$$V_{\text{IF}}(x)=\frac{q}{16\pi\epsilon_s x}, \tag{4}$$

to the solution of Eq. 3: $V(x)$. We find that $\Delta\phi\approx0.30$ eV for the 5% doped diodes. (For the unintentionally doped diode $\Delta\phi\approx0.05$ eV, and thus negligible.) Using the barriers found by the J-V measurements of Fig. 1 and $\phi_{b0}=\phi_b+\Delta\phi$, we obtain for the unintentionally and the 5% doped diodes, $\phi_{b0}=1.05$ eV and $\phi_{b0}=1.1$ eV, respectively. The size of barrier lowering of the 5% doped diode is also consistent with the shape of the reverse current-density trace J_R of the diode (Fig. 1).[2,6] From a plot of J_R of the 5% doped diode against $(V_R+V_{\text{bi}}-k_BT/q)^{0.25}$, where, $(V_R+V_{\text{bi}}-k_BT/q)$ is the total internal voltage that exists across the depletion layer of the diode as in Refs. 2 and 6, we determine: $\phi_{b0}=1.15$ eV and $N_A=5.6\times10^{18}$ cm^{-3}, which is close to the value of the dopant profile of Fig. 3(b) at high reverse bias voltage.

Taking an average full barrier height of $\phi_{b0}=1.1$ eV, the energy diagrams of both diodes can be chosen such that the Fermi energy E_F in the semiconductor is 0.6 eV above the energy of the valence band E_V (Fig. 3, top parts, solid curves). It is remarkable that this energy difference (E_V-E_F) (and V_{bi}) is the same for both unintentionally and 5% doped diodes. Apparently E_F and V_{bi} do not change upon doping and the Fermi level seems to be pinned at 0.6 eV above the valence band. For normal Schottky diodes made on p-type semiconductors, $|V_{bi}|$ should slightly increase with increasing dopant concentration. Various surface and other effects may lead to, for example, Fermi level pinning, which can keep V_{bi} fixed upon doping. We note that this position of E_F in the energy-band gap of the semiconductor agrees well with the position of the first bipolaron band above the valence band that was found for polythiophene.[14] Our observations may thus imply that in our Schottky diodes the Fermi level is pinned by the bulk bipolaron band. This is a first indication of the possible importance of the bipolaron band in the electrical transport in these materials. A hole bipolaron state can only exist on those thiophene oligomers on which charges (holes) are injected or induced by a chemical doping reaction. Since charges are depleted at the metal interface, the bipolaron band cannot exist in the depletion region of the diode, as is schematically drawn in the top parts of Figs. 3(a) and 3(b).

The shift of the J-V curves upon doping is clearly due to the effect of the Schottky-barrier lowering. The full Schottky-barrier height of about 1.1 eV for our diode is in good agreement with the work functions of the metals. For In and Au these work functions are, respectively, 4.1 and 5.1 eV, so that for undoped, pure $T_{12}d_4$ we determine a work function of 4.6 eV.[15] This value is quite reasonable. Brédas *et al.* have estimated, using a valence effective Hamiltonian method, for polythiophene a ionization potential of 5.1 eV.[16] The electron pushing effect of the dodecyl substituents on $T_{12}d_4$ can easily account for the 0.5 eV difference with our experimental value.[17]

It can now be understood that the forward current density of the diodes is limited by the high resistivity of the low doped p^- layer, which leads to SCLC transport at high forward voltages. Apparently, and for unknown reasons, the top layer of the semiconductor is partly undoped during the fabrication process. We are presently investigating this undoping mechanism. The combined presence of a p^- interface and a p^+ bulk layer is, in principle, ideal for obtaining a high current density diode. For applications, it is essential to be able to control this p^- layer in its properties, since it determines largely the diode behavior. The observed mechanism appears to be quite general: We have recently observed a similar rectification mechanism for other Schottky metals, like Pb and Sn, on (doped) $T_{12}d_4$ oligomers.[18]

In conclusion, Schottky diodes fabricated on highly doped thiophene films obtain their rectifying behavior from a partly undoped p^- layer at the metal-oligomer interface with respect to the higher doped p^+ bulk layer. The energy-band diagrams shown explain quantitatively the shape and shift of the J-V curves upon doping and are in full agreement with the C-V measured acceptor density profiles. The diode is best described as a Schottky diode, in which a thin, low conductive p^- layer is present at the interface. This implies a large electric field at the interface which can cause a substantial lowering of the Schottky barrier.

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