

Voltage-Induced Metal-Insulator Transition in Polythiophene Field-Effect Transistors

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We have extensively studied the carrier transport in regio-regular polythiophene field-effect transistors (FETs) from room temperature to 4.2 K. At low temperatures, Zhabrodskii plots ($d \ln \sigma / d \ln T$) demonstrate that the gate voltage and source-drain voltage combine to induce the insulator-to-metal transition at a carrier density of $5 \times 10^{12} \text{ cm}^{-2}$. The carrier transport in the insulating regime is well described by phonon assisted hopping in a disordered Fermi glass with Coulomb interaction between the hopping charge carrier and the opposite charge left behind, as described by Efros and Shklovskii.

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Beginning with the first report of metallic conductivity in a chemically doped conjugated polymer [1], there has been interest in using the gate voltage (V_g) and capacitance in polymer field-effect transistors (FETs) to induce a sufficiently high density of carriers to reach the metallic regime. Carrier mobility (μ) and metallic conduction in semiconducting polymers is generally limited by spatial disorder and the resulting distribution of energies of the localized states in randomly distributed conjugated polymer segments [2]. Consequently, carrier transport is temperature activated with μ typically decreasing strongly for decreasing temperature (T), showing only a nominal decrease in the activation energy for increasing V_g (carrier density) [3]. Eventually, at low T , high tunneling barriers suppress the conductivity in disordered polymers resulting in properties characteristic of an insulator.

Modifications to the molecular structure and new methods of processing have significantly reduced the degree of disorder in state of the art polymer films. FETs made using regio-regular poly(3-hexylthiophene-2, 5-diyl) (RR-P3HT) as the semiconducting polymer give particularly good performance, with μ as high as $0.1\text{--}0.2 \text{ cm}^2/\text{Vs}$ [4,5] at room temperature. The incorporation of regio-regular head-to-tail polymer side chains [4] and optimization of the polymer deposition [5] are principally responsible for the much improved μ . X-ray diffraction studies reveal the formation of self-organized nanocrystalline regions that consist of polymer lamellae with the π - π stacking axis lying preferentially in the transport plane parallel to the substrate surface [4,6]. Therefore, carrier transport in RR-P3HT is unlike that in more disordered polymers, and reflects the degree of electronic coupling among constituent polymer chains.

In this Letter, we study the carrier transport in pristine RR-P3HT FETs (with $\mu \sim 0.1 \text{ cm}^2/\text{Vs}$) at large V_g and high charge densities ($10^{12}\text{--}10^{13} \text{ cm}^{-2}$), over a temperature range from 298 K to 4.2 K. A bottom-contact device geometry incorporating a SiO_2 gate dielectric [5] with typical electric-field breakdown strength $>7.5 \text{ MV/cm}$ [7] is used that has been studied elsewhere using infrared

field-induced charge spectroscopy [8]. Previous studies have characterized the transport in P3HT nanofiber FETs over a more limited T range [9]. By using a field-effect structure, we (i) confine the charge carriers within a narrow region ($\sim 1\text{--}2 \text{ nm}$ thick, approximately a monolayer) near the SiO_2 /polymer interface, and (ii) avoid the effects of extraneous ions introduced by chemical doping. Since the inclusion of charged ions necessarily increases the disorder, use of the field effect minimizes any disruption to the intrinsic density of states [10].

We find that large V_g combined with sufficiently large source-drain voltages (V_{sd}) drives the channel conductance into a weakly T -dependent regime below $\sim 50 \text{ K}$. The data imply a zero-temperature transition from disordered insulator to metal, not reported before in a polymer device. Analysis of the data reveals variable range hopping transport in the insulating regime, with an itinerant attractive Coulomb force between the hopping charge carrier and the opposite charge left behind, as described by Efros and Shklovskii [11].

Devices were fabricated on heavily n -type doped Si substrates supporting a 200 nm thick SiO_2 layer. The source, drain, and gate electrodes were metallized by e -beam evaporation of 50 nm Au with a 5 nm thick Ti adhesion layer. The channel length was $16 \mu\text{m}$ and the channel width was $1000 \mu\text{m}$ for all devices. We use a standard four-probe measurement of the FET channel conductance to account for contact resistance [12] by placing two long parallel electrodes each $2 \mu\text{m}$ wide and $4 \mu\text{m}$ apart inside the channel between the source and drain electrodes. The polymer was deposited by dip coating a 1, 1, 1, 3, 3, 3-hexamethyldisilazane pretreated substrate into a chloroform solution of RR-P3HT (Sigma-Aldrich) at room temperature. Typical film thicknesses were in the range $5\text{--}10 \text{ nm}$. The SiO_2 layer capacitance was measured to be 16.5 nF/cm^2 . Devices were measured using Keithley 2400 SourceMeters (internal impedance $>10^{10} \Omega$). At room temperature, typical on/off ratios were $>10^4$ and the apparent turn-on voltage was $V_g \approx 30\text{--}50 \text{ V}$ [5,13] (gate leakage current was $\sim 1 \text{ nA}$). T was varied between

298 K and 4.2 K by first immersing the device into liquid helium and then slowly raising it above the cryogenic liquid. All conductivities were estimated by assuming carrier confinement to within a thickness of 1 nm near the SiO₂/polymer interface. At low T , the total specific contact resistance was <40 k Ω cm at large V_g , typical for high quality P3HT devices [12].

Figure 1 shows the T dependence of the conductivity for a device with high μ (0.07 cm²/V s) at room temperature. At $V_{sd} = -60$ V [Fig. 1(a)] and large V_g , we clearly identify a weakly T -dependent conductivity for $T < 50$ K that extrapolates to finite conductivity as $T \rightarrow 0$ K, characteristic of metallic conduction. The small ratio of the conductivity (<40) at the highest to lowest T is indicative of weak disorder. For $T > 50$ K, conductivity increases (phonon assisted hopping) with increasing T that is most pronounced at the weakest applied V_g , and is followed by a decrease in conductivity for $T > 200$ K [14].

At large V_g , the current density in the transistor channel was $\sim 10^5$ A/cm² at room temperature. Such a high current performance without noticeable degradation is notable. We found no evidence for significant Joule heating in our devices, as is evident from the voltage-independent peak in conductivity at 200 K, which indicates good thermal contact between the thin polymer film and surrounding

helium reservoir. Moreover, we observed no discontinuity in the apparent conductivity as a function of T when the device was raised above the helium level.

The insets of Fig. 1(a) provide a more sensitive measure of the device data and show a crossover from insulating behavior ($\sigma \rightarrow 0$ as $T \rightarrow 0$) at $|V_g| \leq -40$ V to metallic behavior ($\sigma > 0$ as $T \rightarrow 0$) at $V_g = -150$ V, which implies an insulator-to-metal transition at a critical voltage $V_g \approx -50$ V [5×10^{12} charges/cm² [15]] at low T . The conductivity at this voltage follows a power law with exponent β , i.e., $d \ln \sigma / d \ln T = \beta$, consistent with previous studies of the metal-insulator transition in chemically doped polymers [16]. In these studies, β was less than unity in a wide range of polymers. We find $\beta = 3.3 \pm 0.4$ (given error is 1 standard deviation), which is large by comparison. Note, however, the work of Menon *et al.* was interpreted in terms of a metal-insulator transition in three dimensions and focussed on thick, freestanding polymer samples. The strong carrier confinement expected in polymer FETs suggests that a two-dimensional (2D) model is more appropriate [17]. Our observation of the metal-insulator transition at carrier densities that are much lower than the highest dopant concentrations used in doped polymers ($\approx 3 \times 10^{21}$ cm⁻³ compared to 5×10^{19} cm⁻³ here) is responsible for the relatively lower device conductivity in the metallic regime and consistent with reduced disorder in the pristine (nondoped) polymer.

Figure 1(b) shows the T -dependent conductivity at $V_g = -150$ V and at various V_{sd} . We see behavior similar to that found for varying V_g , with weak T dependence at (and only at) large V_{sd} . Inspection of the double logarithmic and $d \ln \sigma / d \ln T$ plots (insets) reveals critical behavior at $V_{sd} = -24$ V, with insulating or metallic behavior for smaller or larger absolute V_{sd} , respectively. The T dependence in the critical regime is again described by a power law with $\beta = 2.8 \pm 0.8$, equal within experimental error to the value found for varying V_g . Note, as evident from the fitted data in the inset of Fig. 1(b), the critical regime is not exactly at $V_{sd} = -24$ V; therefore, strictly, β here is only an estimate. We also note that the measured data at low T and small V_{sd} (and small V_g) are at least an order of magnitude greater than the experimental resolution, and therefore free of systematic error.

At small V_g and V_{sd} , the conductivity is well described (see fit to the $V_{sd} = -1$ V data in Fig. 1(b), inset) by a T dependence of the form

$$\sigma \propto \exp(-\sqrt{T_0/T}), \quad (1)$$

where T_0 is a characteristic temperature. Similar T -dependent behavior has been identified in heavily doped polymers [16] and attributed to variable range hopping transport with Coulomb interactions, as described by Efros and Shklovskii [11]. We therefore assign the conductivity in our devices at small voltages to Efros-

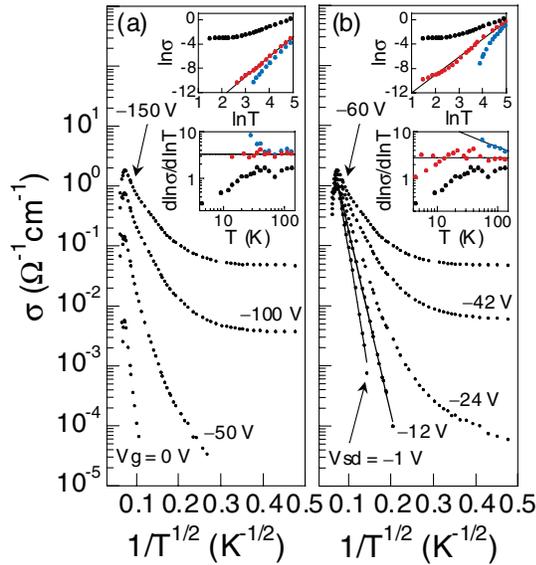


FIG. 1 (color). Conductivity vs inverse square-root temperature for a RR-P3HT FET with $\mu = 0.07$ cm²/V s (a) at $V_{sd} = -60$ V and varying V_g . Top inset is a double logarithmic plot at $V_g = -40$ V (blue), $V_g = -50$ V (red), and $V_g = -150$ V (black). Bottom inset shows the logarithmic derivative (Zabrodskii plot). The straight line is a power-law fit to the $V_g = -50$ V data. (b) At $V_g = -150$ V for varying V_{sd} . The straight lines are exponential fits to the data. Top inset is a double logarithmic plot at $V_{sd} = -1$ V (blue), $V_{sd} = -24$ V (red), and $V_{sd} = -60$ V (black). Bottom inset shows the Zabrodskii plot. The fit to the $V_{sd} = -1$ V data has slope $-1/2$ and the $V_{sd} = -24$ V data are fitted to a power law.

Shklovskii transport in a disordered Fermi glass, where carriers hop between randomly distributed localized sites.

In two dimensions, T_0 is given by [11]

$$T_0 = \frac{Ce^2}{4\pi\epsilon_0\epsilon_r ak_B}, \quad (2)$$

where a is the localization radius of the carrier wave function, e is the electronic charge, ϵ_0 and ϵ_r are the vacuum and relative dielectric constants, respectively, k_B is the Boltzmann constant, and $C \approx 0.6$ [18]. We find that T_0 decreases from 9963 K to 4899 K [fitted data in Fig. 1(b)] as $|V_{sd}|$ increases from $V_{sd} = -1$ V to $V_{sd} = -12$ V, consistent with the approach to a voltage-induced phase transition (identical behavior is found when varying V_g at fixed V_{sd}). Using Eq. (2) (with $\epsilon_r = 3$), we get $a \approx 0.7$ nm at $V_{sd} = -12$ V, which is approximately equal to the size of a single polymer repeat unit (monomer) and equivalent to twice the distance between face-to-face packed thiophene rings [6]. Note the spatial extent of the carrier wave function is within the structural coherence length measured in partially ordered regions in polythiophene films [19]. As the charge density increases (increasing V_g) at constant V_{sd} , the carrier wave functions in the more highly ordered regions will begin to overlap. A weakly metallic state is formed at the highest charge density ($\approx 1.5 \times 10^{13}$ cm $^{-2}$, $V_g = -150$ V, which corresponds to a mean carrier spacing of 2.6 nm); assuming a 2D density of states (zero order approximation), we estimate the Fermi energy, $\epsilon_F \sim 37$ meV, a value that is consistent with the increase in conductivity found for $T > 50$ K at large V_g (Fig. 1).

Figure 2 shows the T -dependent conductivity for a relatively low- μ (0.02 cm 2 /V s) device, fabricated in a differ-

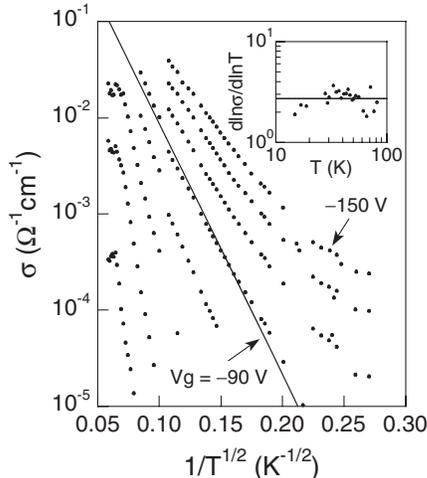


FIG. 2. Conductivity vs inverse square-root temperature for a device with $\mu = 0.02$ cm 2 /V s at $V_{sd} = -60$ V and varying V_g (-20 V steps) between $V_g = -10$ V and $V_g = -150$ V. The straight line is an exponential fit to the $V_g = -90$ V data. Inset shows the logarithmic derivative of the conductivity at $V_g = -150$ V. The straight line is a power-law fit to the data.

ent batch to the device shown in Fig. 1, with, presumably, a disparate polymer layer. The data indicate that no insulator-metal crossover exists for this device up to the largest applied V_g . Instead, at the largest V_g , the conductivity exhibits power-law behavior with an exponent equal to $\beta = 2.7 \pm 0.5$ (Fig. 2, inset), similar to that found in the critical regime of the higher mobility polymer. The large ratio of the conductivity (>100) at the highest to lowest T is indicative of increased disorder, which thus identifies the metal-insulator transition as being driven by structural disorder within polymer chains [20]. At $V_g = -90$ V, $a \approx 0.9$ nm (Fig. 2, fit), which is comparable to that found in the higher μ device. Therefore, it is apparently the larger-scale (>1 nm) disorder that is sufficient to prevent crossover to the metallic regime in the low- μ device.

Figure 3 shows the source-drain electric-field (E) dependence of the conductivity for a high- μ device at low T in the metallic regime (large V_g and V_{sd}). The conductivity exhibits a field dependence of the form

$$\sigma \propto \exp(-\sqrt{E_0/E}) \quad (3)$$

up to the highest field applied across the channel (50 kV/cm), where E_0 is a constant. This strongly field-dependent behavior in the weakly T -dependent regime is expected for Efros-Shklovskii hopping transport in the limit $eEa \gg k_B T$, as recently found in thin films of semiconductor nanocrystals [21]. Detailed analysis of all our devices revealed the same field dependence given in Eq. (3). Thus, over a wide range of E , short-range screening is ineffective, consistent with $2a$ being smaller than or comparable to the carrier spacing in the weakly metallic regime.

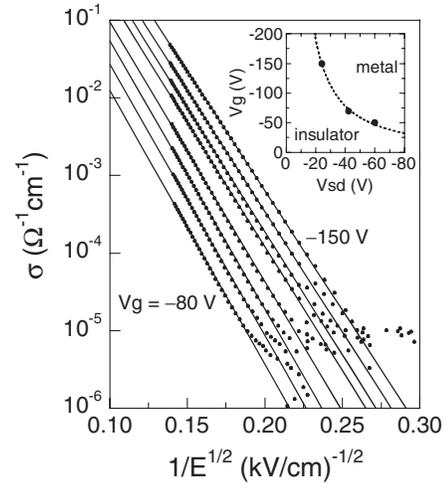


FIG. 3. Conductivity vs inverse square-root electric field for a device with $\mu = 0.08$ cm 2 /V s at 12.4 K with varying V_g (-10 V steps). The straight lines are exponential fits to the data. The electric field across the transistor channel is the measured four-probe voltage divided by the effective channel length. Inset shows V_g vs V_{sd} in the critical regime for the device shown in Fig. 1. The dashed line is a guide to the eye.

The inset of Fig. 3 shows how the metallic regime is reached by a combination of V_g and V_{sd} such that at fixed V_g , V_{sd} drives the conductivity to a critical threshold beyond which extended (delocalized) states are formed. From the capacitance relation, the total density of occupied states that are delocalized is given by $\Delta n = C_{ox}|V_g - V_c|f(V_{sd})$, where C_{ox} is the gate capacitance per unit area, V_c is the critical gate voltage, and $f(V_{sd})$ is the fraction of the total number of pathways that become delocalized by the source-drain field. In the insulating regime, $f = 0$ and hence $\Delta n = 0$. Thus, as confirmed by the strong dependence of the conductivity on V_{sd} (Fig. 3), $f \ll 1$ even at large V_g and V_{sd} . Alternatively, from the relation $\sigma = ne^2\tau/m_e$, where n is the charge density, τ is the scattering time and m_e is the mass of an electron, at $V_g = -150$ V and $V_{sd} = -60$ V, $\sigma = 0.1 \Omega^{-1}\text{cm}^{-1}$ implies that $\tau \sim 10^{-17}$ s at 4.2 K. This is at least 2 orders of magnitude less than that typically observed in doped metallic polymers [22], hence $f < 0.01$ and the mobility of carriers in extended states must be $\approx 1/f$ times larger than that measured. We therefore conclude that only a small fraction of the field-induced charge contributes to metallic conduction, with most charges occupying localized states at lower energies, consistent with a mobility edge in the density of states.

In the conventional description proposed by Mott [23], for energies below the mobility edge (ϵ_c) all states are localized. For energies approaching ϵ_c , however, a increases and diverges at ϵ_c . For energies greater than ϵ_c , the states are extended. If occupied, such delocalized states would lead to metallic behavior. In the simplest picture then, the insulator-metal transition will occur when $\epsilon_F > \epsilon_c$, with occupied extended states near ϵ_F . As implied by the inset of Fig. 3, $\epsilon_F < \epsilon_c$ but sufficiently close to ϵ_c that the transition to the metallic regime can be driven by V_{sd} .

Finally, we can roughly estimate the height of the tunneling barrier ϕ_b between occupied localized states, with energies close to ϵ_c (nearly extended) but distributed randomly in space, from a simple tunneling approximation. For $E = 0$, the barrier width at which the carrier wave function falls off to $1/e$ is given by $b = (2m_e\phi_b/\hbar^2)^{-1/2}$, where \hbar is the Planck constant divided by 2π . Thus, using $b = 2a \approx 1.4$ nm, the dominant barrier height is, approximately, 19 meV. This barrier height can be compared with the energy difference across the barrier due to the external electric field from which $\Delta\epsilon = eEb$ and $E = 20$ kV/cm (Fig. 1) is 2.8 meV in the critical regime. Then, E lowers the tunneling barrier and increases the transmission probability, $p \approx \exp\{-2[(\phi_b - \Delta\epsilon)/\phi_b]^{1/2}\}$. For $\phi_b = 19$ meV, $p \approx 0.16$ at the critical V_{sd} . The Coulomb interaction is not included in this simple estimate. However, screening of the local internal field by the more extended states will effectively increase the field across the barrier and thus increase p above that estimated. In this description, $p \rightarrow 1$ corresponds, approximately, to the insulator-to-metal transition.

We have identified an insulator-to-metal transition in RR-P3HT FETs. Even at field-induced charge densities of $\approx 5 \times 10^{12} \text{ cm}^{-2}$, the crossover to the metallic regime requires a significant V_{sd} ($E \approx 20$ kV/cm). Electric-field assisted carrier tunneling through randomly distributed potential barriers further delocalizes occupied states, driving the conductivity into the metallic regime. Analysis of the data indicates that a small fraction (< 0.01) of the field-induced charge carriers occupy delocalized states. Efros-Shklovskii hopping transport with Coulomb interactions is identified from the T -dependent conductivity in the insulating regime. At high carrier densities, improved structural ordering in the semiconducting polymer film enables metallic transport. We find high current densities ($\sim 10^5$ A/cm²) for device operation without noticeable degradation, which is encouraging in the context of potential applications for polymer FETs.

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