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Electronic transport in conducting polymer nanowire array devices

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Abstract
We report on the temperature dependent conductivity and current–voltage (I–V) properties of novel polyaniline nanowire array devices. Below 60 K, I–V measurements show a transition to non-linear behaviour, leading to the onset at 30 K of a threshold voltage, for potentials below which little current flows. By considering an intrinsic morphology of small conducting regions separated by tunnel junctions, we show that charging of the conducting regions leads to Coulomb blockade effects that can account for this behaviour.

S Online supplementary data available from stacks.iop.org/Nano/22/105202/mmedia

1. Introduction

Conducting polymers are complex materials with a structural morphology that depends upon many factors; including the sizes of the monomer and the dopant, conformation of the polymer chains, polymer branching and defects in the conjugation. In spite of this complexity, improvements in synthesis strategies have led to polymers with metallic-like signatures, as clearly evidenced by the metal–insulator transition (MIT) in the temperature dependent conductivity and a finite density of states at zero temperature [1, 2]. Measurements of the temperature dependent thermoelectric power [3], low temperature specific heat [4], Pauli susceptibility [5, 6], optical conductivity [7], and observations of crystallinity in x-ray diffraction [8] and scanning force microscopy [9], also support this conclusion. The origin of the MIT has focused on two main interpretations, a homogeneous [10] '3D Anderson localization' disorder-induced MIT in which a mobility edge in the density of states separates states localized by disorder from delocalized states, and alternatively, an inhomogeneous [11] or heterogeneous [12] morphology driven MIT, where the material is composed of semi-crystalline high conductivity regions that are interspersed with disordered or amorphous regions with low conductivity. Additionally, there is growing interest on the origin of non-linear I–V properties at low temperature in some conducting polymers, with interpretations including a transition from a Luttinger liquid/Wigner crystal at high temperature to Coulomb blockade behaviour at low temperature [13, 14], and thermal activation/fluctuation-induced tunnelling at high temperature with a transition to Zener-type tunnelling at low temperature [15]. Phonon-assisted tunnelling [16] and non-Ohmic 3D variable range hopping [17] models have also been used to explain non-linear I–V curves as well as inelastic co-tunnelling in the Coulomb blockade regime, as observed in quantum dot nanoparticle systems [18, 19]. Of particular relevance also is work on 1D arrays of conducting islands, where a scaling law of conductance on temperature and voltage has been observed in semiconductor nanowires and multiwalled carbon nanotube systems [20]. Theoretical work has shown the importance of co-tunnelling processes in these systems, accounting well for the observed power law behaviour as well as $G = \exp(-(T_0/T)^{(-1/2)})$ behaviour that is observed in many systems [21].

In this paper, we report on Coulomb blockade behaviour in polyaniline nanowires, which arises from the heterogeneous morphology of the polymer. Transport measurements made on the polymer nanowires, show a transition from Ohmic behaviour at room temperature to non-linear I–V behaviour at low temperatures and exhibit a threshold voltage below 30 K. We show that a model consisting of a 1D array of N tunnel junctions, can account for the experimental I–V data and predict a reasonable size for the conducting regions.

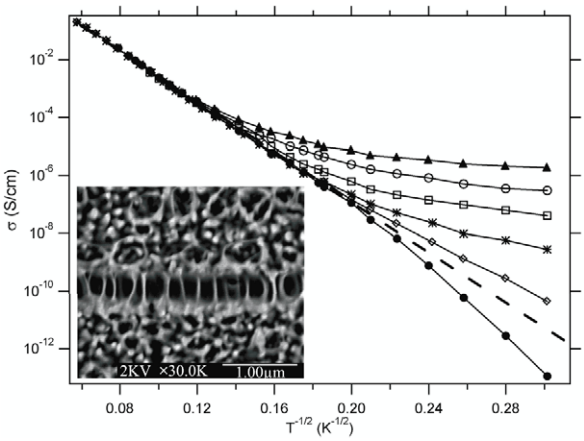

Figure 1. Plot of σ versus $T^{-1/2}$ on a log plot for applied voltages of 6 V (▲), 4 V (○), 2 V (□), 0.5 V (✱), 0.25 V (◊) and zero bias conductance (●) measurements. The straight dashed line (- - - -) illustrates consistency at high temperatures with the hopping model (equation (1)) for $\gamma = 1/2$. Inset: nanowires spanning a 500 nm gap between two gold electrodes.

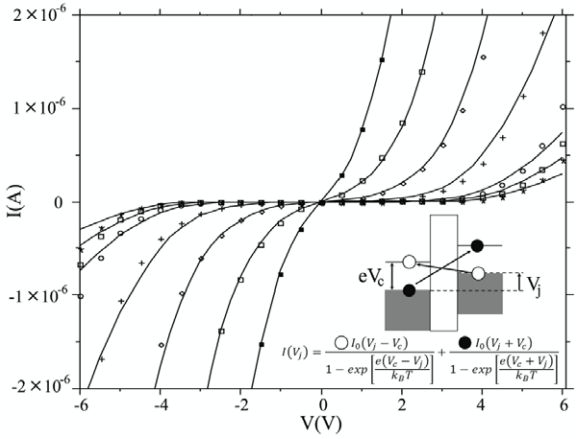

Figure 2. Current versus voltage of the nanowire device at 11 K (✱), 15 K (□), 20 K (○), 30 K (+), 40 K (◊), 50 K (□) and 60 K (■). The straight lines are fits to equation (2). Inset: schematic of a single tunnel junction with charging eV_c and potential bias V_j and showing how the total tunnel current I (Vj) arises from two contributions (● and ○).

2. Experimental details

The nanowire devices [22] were fabricated using an *in situ* growth and patterning technique [23] based on a template free electrochemical method [24, 25]. A typical device consists of approximately 1000 parallel nanowires bridging two gold contacts with a separation 500 nm (inset figure 1). Nanowires perpendicular to the gold pad surface are also present but play no role in the electrical properties of the device since they do not bridge the gap between the two electrodes. Measurements down to 11 K were made in a vacuum cryostat ($P \sim 10^{-6}$ T) using a Keithley 2400 SMU in a two-probe geometry. Conductivity was calculated using the following parameters: number of nanowires (1000), nanowire diameter (50 nm), nanowire length (500 nm).

3. Results and modelling

In figure 1, the conductivity at temperatures 11–300 K, and for different applied voltages is plotted versus $T^{-1/2}$. The near linear correlation at temperatures above 60 K suggests a Mott's variable range hopping (VRH) [26] mechanism, equation (1), which has commonly been used to describe transport in conducting polymers in the insulating state. The room temperature conductivity, 0.2 S cm^{-1}, and value of $T_0 = 11.14 \times 10^3$ is typical of the lower conductivity polyaniline types [27].

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{\gamma}] \quad (1)$$

where σ_0 has a much weaker temperature dependence than the exponential term, T_0 is a parameter depending (inversely) on the localization length and on the density of states near the Fermi level, and γ is equal to $(n + 1)^{-1}$, with n the dimensionality of the hopping.

Although VRH has often been used to describe transport for conducting polymers on the insulating side of the MIT, a $\ln\sigma$ versus $T^{-1/2}$ dependence occurs for a number of models that can also describe transport in conducting polymers, including quasi-1D-hopping [28], correlated hopping between polaronic clusters [29], 3D hopping in the presence of electron–electron interactions [30] and tunnelling between mesoscopic metallic islands [31]. Thus from this data alone it is difficult to discriminate experimentally between models, and we instead focus on the I–V measurements at low temperature.

Below 60 K, a transition to non-linear behaviour is observed in the I–V measurements (figure 2). The effect increases with decreasing temperature so that at 30 K a threshold voltage exists, V_t, below which only very little current flows. With further decreases in temperature, V_t increases from 0.5 V (at $T = 30$ K) to 3.5 V (at $T = 11$ K). A similar transition to non-linear I–V behaviour at low temperatures with a threshold voltage was also reported in polyacetylene nanofibres, being interpreted as a transition from a 1D Luttinger liquid to Coulomb blockade behaviour [13]. The onset of a threshold voltage at 30 K in our polyaniline nanowire devices is also evident in the zero bias conductance measurements, figure 1, which indicate a transition to a much stronger temperature dependence below 30 K than that expected for VRH hopping-type behaviour.

To explain the non-linear I–V behaviour, we assume the dominant mechanism at low temperature is Coulomb blockade. Our reasoning is based upon the morphology of conducting polymer systems, being composed of both crystalline and non-crystalline regions, and the strong similarity of the transport properties with previously observed Coulomb blockade behaviour in carbon [32] and metal [33, 34] nanoparticle systems, namely a transition to non-linear I–V dependence and the appearance of a threshold voltage at low temperature. To interpret the data we have treated the morphology of the polymer nanowires as heterogeneous, consisting of small conducting regions separated by insulating tunnel barriers, and have used a model based on Coulomb blockade in a 1D array of N tunnel junctions [35, 36]. Here, equation (2) describes

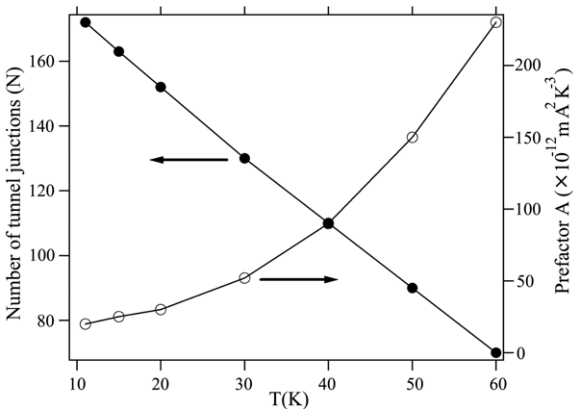

Figure 3. Number of tunnel junctions (●) and the junction transparency (○) versus temperature for the fits in figure 2.

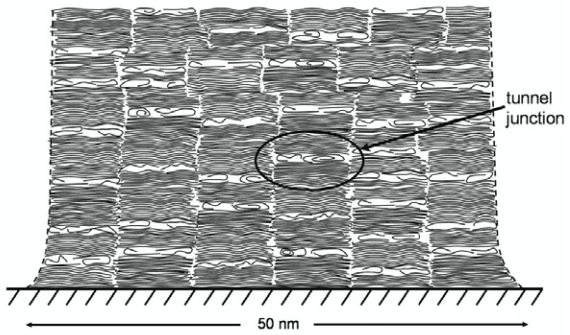

Figure 4. Schematic of the morphology of polymer chains within a polyaniline nanowire and the formation of tunnel junctions.

the current through a series of N identical tunnel junctions as a function of the applied potential (V). V/N is the voltage drop on one of the junctions, and $eV_C = e^2/C$ is the charging energy of the confined conducting regions. Equation (3) defines the non-interacting current through the tunnel junction separating two conducting regions with chemical potential μ and junction transparency related to A. We assume the conducting regions are metallic-like with a density of states that varies as $|E - eV|^{1/2}$. The conduction process for a single junction is illustrated schematically in the inset to figure 2. (Note: a 2D array of N tunnel junctions is also a possible model for our multi-nanowire device but the I–V curves were not consistent with our experimental data.)

$$I(V) = \frac{I_0(V/N - V_C)}{1 - \exp[\frac{e(V_C - V/N)}{k_B T}]} + \frac{I_0(V/N + V_C)}{1 - \exp[\frac{e(V_C + V/N)}{k_B T}]} \quad (2)$$

$$I_0(V) = \frac{A}{k_B^3} \int \mathrm{d}E \sqrt{|E - eV - \mu|}\sqrt{E - \mu} \times \left(\frac{1}{1 + \exp[\frac{E - eV}{k_B T}]} - \frac{1}{1 - \exp[\frac{E}{k_B T}]} \right). \quad (3)$$

The experimental data were fitted by adjusting the parameters A, V_C and N (with $\mu = 0$ for zero gate voltage) for each of the I–V traces. By assuming a constant Coulomb gap energy it was found that N and A had to be variable with temperature. The value of $eV_C = 18$ meV was found to match best the Coulomb gap present at both 11 and 60 K, while N and A were varied until χ^2 was minimized for each curve fit. Good fits were obtained, as shown by the solid lines in figure 2 (see supporting information for the same fits on a log scale, figure a available at stacks.iop.org/Nano/22/105202/mmedia), and clear trends with temperature for N and A, as shown in figure 3. We note here that variable range hopping in the presence of strong electric fields was disregarded as a suitable model since the conductance is not temperature independent at low temperature and high field values (see supporting information, figure b available at stacks.iop.org/Nano/22/105202/mmedia).

This modelling suggests the nanowires have a heterogeneous morphology, as is similarly the case for polyacetylene fibrils [37] and many bulk polymer films [38]. The morphology in this case consists of small conducting regions separated by nanoscale tunnel barriers, similar to that shown in figure 4. Here, the polymer chains, lying parallel to the substrate, as shown by FTIR studies [24], form small highly ordered regions with high conductivity. The size of the conducting regions are estimated to be approximately 30 Å by using the average length of the nanowires, 500 nm, and the number of conducting regions at low temperature, $N = 172$. This size is similar to the crystalline domain length in bulk polyaniline [39] films, 50 Å, and corresponds to approximately nine polymer chains given a typical interchain separation distance of 3.5 Å. The small tunnel junctions between the conducting regions are likely the result of more disordered polymer chain growth, possibly due to defects in conjugation or different polymer conformation. It is known that, in contrast to extended chain conformation, the closed coil conformation gives more disordered growth and poorer electrical properties in polyaniline [40]. These regions are likely to be small, forming tunnel junctions at low temperature whilst allowing transport from thermally activated hopping processes at high temperatures. This can be seen from the variation of N and A with temperature. At 11 K the number of tunnel barriers (N) is approximately 172. However, this decreases to 70 as the temperature is increased to 60 K, indicating that at higher temperatures some of the junctions are rendered transparent by thermal activation processes. This agrees well with the corresponding increase in the average transparency of the junction (A) from 20×10^{-12} mA^2 K^{-3} to 230×10^{-12} mA^2 K^{-3}. From the Coulomb gap energy, 18 meV $= e^2/2C$, the average capacitance of the islands is 4.4×10^{-18} F. Approximating the islands as oblate metallic spheroids dispersed within a non-conducting polymer ($\varepsilon_r = 5.0$) and assuming an average tunnelling distance of 3 Å, gives a value for the average diameter of the islands (minor axis) as 32 Å. This is in good agreement with the size of the islands that was calculated from the number of tunnel junctions.

4. Conclusions

In conclusion, we have measured the temperature dependent conductivity and I–V characteristics of polyaniline nanowires bridged between gold electrodes. The data indicates conduction dominated by thermally activated processes at high

temperatures with a crossover to Coulomb blockade transport at low temperatures, similar to that expected in weakly coupled quantum dot systems [41]. Modelling in terms of a 1D array of N tunnel junctions indicates consistency with a heterogeneous model for the polymer morphology. The finding of a heterogeneous morphology in polyaniline nanowires indicates that controlling the polymer chain morphology should provide a route to polymers with better electrical properties for device applications.

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