Direct measurement of charge transport through helical poly(ethyl propiolate) nanorods wired into gaps in single walled carbon nanotubes

Nan Wang\textsuperscript{1,5}, Koji Yano\textsuperscript{1,2,3}, Colm Durkan\textsuperscript{1,6}, Natalie Plank\textsuperscript{1}, Mark E Welland\textsuperscript{1,6}, Yan Zhang\textsuperscript{4,5}, Husnu Emrah Unalan\textsuperscript{4}, Mark Mann\textsuperscript{4}, G A J Amaratunga\textsuperscript{4} and William I Milne\textsuperscript{4,6}

\textsuperscript{1} Nanoscience, University of Cambridge, 11 J J Thomson Avenue, Cambridge CB3 0FF, UK
\textsuperscript{2} Canon Europe Ltd, 11 Roundwood Avenue, Stockley park, Uxbridge UB11 1JA, UK
\textsuperscript{3} Canon Research Centre, 3-30-2, Shimomaruko, Ohta-ku, Tokyo, 146-8501, Japan
\textsuperscript{4} Centre of Advanced Photonics and Electronics, Department of Engineering, University of Cambridge, 9 J J Thomson Avenue, Cambridge CB3 0FF, UK

Received 18 November 2008, in final form 16 January 2009
Published 16 February 2009
Online at stacks.iop.org/Nano/20/105201

Abstract
We report the direct measurement of electrical transport through rod-like polymer molecules, of poly(ethyl propiolate) (PEP), utilizing single walled carbon nanotubes (SWNTs) as electrodes. The electrical properties of the devices were measured (i) before cutting a SWNT, (ii) when a SWNT was cut and (iii) after PEP deposition into the nanoscale gap in a cut SWNT. The gate-dependent electrical properties showed a reduction in current from $I_{\text{on}} = 2.4 \times 10^{-7}$ A for SWNT devices to $I_{\text{on}} = 3.6 \times 10^{-9}$ A for PEP bridge devices, both with the ON/OFF ratio of $10^4$. Similarly, metallic SWNT devices showed a reduction in current from a few hundreds of $\mu$A for a SWNT device to a few nA for a PEP–SWNT structure. The current density of a single PEP molecule is $10^5$–$10^6$ A cm\textsuperscript{-2}, which is relatively high, indicating that the PEP molecule can carry significant current. Use of SWNT electrodes was seen to be an effective method of contacting PEP nanorods to facilitate electrical measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
In recent years, there has been intense interest in organic semiconductors, driven by their potential use in large area, flexible and low-cost devices [1–5]. Soluble organic semiconductors, or polymer semiconductors have been studied mostly due to their compatibility with solution processes such as inkjet printing, screen printing and roll to roll processing [6–8] for light emitting diodes (LED), field effect transistors (FETs), and RFID tags etc.

Electrical properties of polymers are usually measured in their bulk form where the complicated morphology of the polymer bulk materials and inter-chain coupling effects hinder the intrinsic electrical characteristics of the molecules themselves. Although isolation of an individual polymer chain still remains a challenge, it is necessary in order to obtain a better understanding of electron transfer at the molecular scale. This approach is also important from the view of molecular electronics, in which electronic circuitry is reduced to molecular dimensions.

The second challenge is the establishment of suitable contacts between the target molecules and the metal electrodes. Self-assembly techniques [9–12] could potentially be used. However, structural modification of the small channel region together with large electrode areas makes this difficult in practice. Using individual single walled carbon nanotubes (SWNTs) to form nanoscale contacts is an alternative approach, utilizing the small size and high electrical conductivity. In addition, standard SWNT field effect transistor...
(SWNT-FET) fabrication technology allows easy fabrication of these contacts [13–15]. Another advantage of using SWNTs is that they provide very low profile electrodes and prevent the bending of the molecule near the electrode junction.

Polyacetylene (PA) is well known as the first organic conducting polymer discovered which has a high conductivity comparable to copper. However, its instability has limited its application and usefulness [16, 18]. Unlike conventional polyacetylene [17–19], Helical polyacetylene (HPA) has a helical –C=C– backbone structure [20] and is therefore expected to have physical characteristics different to those of conventional polyacetylenes. HPA was found to have a different stiffness and stability depending on the side chain. One of the HPAs, poly-ethylpropionate (PEP) was studied here due to its rod-like structure and good stability. The structure of PEP used in this work is presented in figure 1. From its structure, PEP is expected to have a conducting core surrounded by an insulating shell of side chain molecules, therefore forming ideal molecular wires. However, there are only two recent reports on the electrical property of HPA which have shown the conductivity of the bulk film structure with gaps wider than molecule length [21, 22]. In this paper, PEP nanorods were attached across a nanosized gap generated in a SWNT and the electrical property of PEP was studied at the molecular level. The combination of CNT junction and HPA are thought to bring an ideal device structure for single molecular electronics. Due to the fact that the electrical characteristics of the HPA can be tuned by modifying the side chains, this opens up the possibility of a wide range of possible device functions; more so than can be achieved through SWNTs alone.

2. Experimental details

The PEP nanorods used here have a helically structured –C=C– backbone and –COOCH₂CH₃ side chains. The average molecular weight (Mₘ) and polydispersity ratio (Mₘ/Mₚ) of the PEP nanorods were found to be 80 900 and 1.73, respectively. Helical PEP nanowires were dissolved in chloroform with concentrations of 0.01 or 0.1 mg ml⁻¹, and then sprayed onto a freshly prepared gold (111) surface for AFM imaging. The gold surface was prepared by e-beam evaporation of gold onto a mica surface at a pressure of 10⁻⁷ mbar, followed by subsequently flame-annealing with hydrogen in air. AFM observations were carried out at room temperature with commercial instruments (Digital Instruments (DI), Nanoscope IIIA, Dimension 3000 and Multimode). Tapping mode AFM images were taken under ambient conditions.

For transport measurements, SWNT-FETs were fabricated with a bottom gate configuration. Degenerately n-doped silicon was used as the substrate with a 1 µm thermal oxide layer as the dielectric layer. SWNTs were grown by chemical vapour deposition (CVD) using acetylene (C₂H₂) gas as the carbon feedstock. Lithographically defined triple-layer metal thin films (10 nm Al/1 nm Fe/0.2 nm Mo) [23] were used as the catalyst for site selective SWNT growth. SWNTs were grown at 900°C for 15 s. Following growth, source and drain electrodes, made of Au (50 nm)/Cr (3 nm), were fabricated using electron beam lithography, sputtering and lift-off processes. In order to form a gap in the SWNTs, a 20 V DC bias was applied between the source and drain electrodes and gate voltage of −16 V was applied to open the channel in the semiconducting SWNTs during the voltage application. The resulting high current causes a section of the SWNT to burn, leaving a nanoscaled gap. AFM investigations on approximately 100 samples revealed that the size of the gap is between 5 and 60 nm. PEP nanorods were then sprayed onto the cut SWNT device from a chloroform solution with a concentration of 0.1 mg ml⁻¹. A schematic diagram of the chemical structure of the PEP nanorods and the device configuration is shown in figure 1. Electrical measurements were made at each step (before and after cutting SWNTs, and after PEP deposition) using an HP 4156 semiconductor parameter analyzer.

3. Results and discussions

Figure 2(a) shows typical AFM images of PEP nanorods on a Au(111) surface deposited from a chloroform solution. The diameters of the PEP nanorods are measured to be in the range of 1–2 nm and their lengths are in the range of 50–120 nm. Isolated PEP nanorods can be seen in...
Figure 2. (a) A typical AFM image of PEP on Au(111) surface deposited from a solution with a concentration of 0.01 mg ml\(^{-1}\), showing an individual PEP nanorod. (b) AFM image of the similar sample but prepared with higher concentration (0.1 mg ml\(^{-1}\)) which is used for device structures with SWNT.

Figure 3. (a) SEM image of a pristine SWNT-FET device with Cr/Au source and drain electrodes. (b) AFM image of a cut SWNT. The diameter of the SWNT is \(\sim 1\) nm and the size of the gap is \(\sim 15\) nm.

In this figure the bright regions show the rod-like structure of PEP. We believe this to be due to the side chain, –COOCH\(_2\)CH\(_3\), effectively isolating the molecule to maintain a rod-like morphology. In addition, the morphology of the nanorods on the Au surface was found to be stable for weeks, which is attributed to side chain encapsulation. Figure 2(b) shows an AFM image of a similar sample but prepared with higher concentration (0.1 mg ml\(^{-1}\)) of PEP which is used for device structures with SWNT. The density of the PEP nanorods covering the Au surface has increased significantly, therefore also increasing the chance of forming a bridge across the gap in the SWNT.

A SEM image of a pristine SWNT-FET device is shown in figure 3(a). Due to the preparation of the SWNT devices, there are usually several SWNTs in the vicinity of the device; however, only one or two SWNTs are completely bridging the source and drain electrodes, as shown in the figure 3(a). Following SWNT growth and deposition of contact metals, a nanoscale gap was introduced into SWNTs by current breakdown on electrical ‘burn off’ technique [24]. Upon voltage application, power is not distributed uniformly along a SWNT due to defects. These defect sites (such as kinks or dislocations) have higher resistance and hence dissipate more power under the application of a voltage. They form hot spots which eventually lead to electrical breakdown, inducing a gap in SWNTs [24]. For the particular sample described here, the induced gap is \(\sim 15\) nm wide, as shown in figure 3(b).

It is well known that defect free sidewalls and caps at the end of SWNTs have excellent chemical stability. However, SWNTs form open ends by electrical breakdown, producing free unsaturated carbon bonds, which make them hydrophobic and capable of acting as anchoring sites for reactive species [25]. Therefore, foreign species favourably attach to the cut ends of SWNTs. In the PEP structure, both single and double bonds occur in the polymer backbone, both of which are hydrophobic, similar to the –COOCH\(_2\)CH\(_3\) side group.
This makes the PEP nanorod compatible with the hydrophobic, cut ends of the SWNT. Therefore, following the deposition of PEP nanorods from solution, a physical contact forms between cut SWNT ends and the PEP nanorods rather than a chemical contact formed on oxygen plasma cut SWNTs as has been studied by Gao and co-workers [13].

After dispersing the molecules, devices were imaged again with AFM and electrical measurements were conducted to confirm the presence of the nanorods in the gap. Due to the roughness of the SiO2 surface, which is larger than the diameter of the PEP molecules, it is difficult to obtain a clear AFM image of the PEP molecules. Despite this, it was possible to observe traces of the PEP molecule bridging the gaps in a SWNT, which is similar in appearance to that observed for PEP on gold. The attached supporting material shows the PEP molecule over the SWNT gaps. We further confirmed the bridge of PEP using the electrical characterization. Although the SEM image indicated that FET devices are often consisting of more than one SWNT, usually only one SWNT gap was bridged with PEP nanorods. Therefore, despite the presence of multiple gaps, electrical characteristics were obtained from a single or a small number of PEP nanorods.

Electrical measurements were conducted at room temperature under ambient conditions. The gate transfer characteristics of a pristine SWNT-FET device is shown (black curve) in figure 4(a). The $I-V$ characteristics for this device show for $V_{ds} = 1 \text{V}, V_g = -20 \text{V}$, ON current $I_{on} = 2.5 \times 10^{-7} \text{A}$, OFF current $I_{off} = 3.3 \times 10^{-11} \text{A}$, so that the ON/OFF ratio is $\sim 10^4$ with a threshold voltage of $\sim -5 \text{V}$. The blue curve in figure 4(a) shows the transfer characteristic of the same device following current breakdown. There is no measurable conductance down to the noise limit of the measurement setup. The red curve in figure 4(a) shows the transfer characteristic of the device after PEP nanorod deposition on SWNT electrodes: at $V_{ds} = 1 \text{V}, V_g = -20 \text{V}$, the ON current $I_{on} = 3.6 \times 10^{-9} \text{A}$, and OFF current $I_{off} = 3.8 \times 10^{-13} \text{A}$ so that the ON/OFF ratio is still $\sim 10^4$ with a threshold voltage $\sim -6 \text{V}$. Interestingly, this result implies that the bridged gaps partially recovered their p-type gate-dependent electrical characteristics, indicating that single PEP molecules are conductive.

In fact, using the fabrication process outlined above, two different device behaviours have been observed. Figure 4(b) shows gate-dependent output characteristics of a SWNT-FET after PEP nanorod bridging, whilst figure 4(c) shows a similarly fabricated device showing no gate dependence. This difference could be attributed to the nature of the reconnected SWNTs being semiconducting or metallic. Independent of the nature of the SWNTs, both devices show a significant reduction of current as compared to their pristine states as shown in figure 4(a). Figure 4(b) shows the output characteristics of a PEP nanorod bridging a semiconducting SWNT at different gate voltages. There is a significant difference in the gate-dependent current, ranging from 0.5 $\mu\text{A}$ at $V_g = -16 \text{V}$ (when the semiconducting nanotube is ON), to a few nA at both $V_g = 0$ and $+16 \text{V}$. The current decreased from $\sim 180 \text{nA}$ to $\sim 2 \text{nA}$ at $V_g = +16 \text{V}$.

Figure 4. Electrical measurements of SWNT-FETs: (a) the gate transfer characteristics before SWNT cutting, after cutting, and following PEP nanorod bridging; (b) output characteristics of a PEP nanorod bridging a semiconducting SWNT; (c) output characteristics of a PEP nanorod bridging a metallic SWNT.
for the semiconducting SWNT to \(~\sim 2.5\) nA for the PEP nanorod bridged semiconducting SWNT at \(V_G = -16\) V with a drain–source voltage of 1 V, as shown in figure 4(a). By contrast, figure 4(c) shows typical \(I–V\) characteristics of a PEP nanorod bridging a metallic SWNT. Although the current has decreased from a few \(\mu\)A for the pristine metallic SWNT to \(~\sim 7\) nA for the PEP nanorod bridged metallic SWNT at \(V_G = 1\) V, the device shows identical transfer characteristics at \(V_G = -16, 0\) or +16 V. These results also suggest that PEP nanorods are conductive. However, such a reduction in current for the PEP nanorod bridged SWNTs in comparison to the pristine SWNTs, implies that the resistance of SWNT-PEP nanorod device increases. A further investigation is necessary to find out the mechanism causing the increase in the resistance.

To confirm that the measured electrical characteristics originated from the PEP molecules, we performed control experiments where only chloroform was deposited onto the nanoscale gap. No current was measured from those devices which excludes parasitic effects and proves that the results are purely from PEP nanorods. Throughout the course of this work more than 100 SWNT junctions were prepared and the yield of PEP attachment was found to be around 10%. This low yield could be due to the mismatch between the size of the SWNT gap and the length of the PEP nanorods, as well as to the fact that the deposition of PEP is not directed in any way.

At this stage we refrain from mobility calculations due to difficulties in extrapolating the results. The current levels of SWNT-PEP devices were typically in the range of \(10^{-8}–10^{-9}\) A at \(V_{DS} = 1\) V. Assuming that the current flows through a single molecule of diameter 1 nm, the corresponding current density of the PEP nanorod is \(~\sim 10^{5}–10^{6}\) A cm\(^{-2}\), which is comparable to that of metals \((~\sim 10^{5}\) A cm\(^{-2}\)); however, this is still much lower than that of carbon nanotubes \((~\sim 10^{9}\) A cm\(^{-2}\)). This indicates that the PEP molecule can carry significant currents and is a promising nanowire material. This is in good agreement to the recent paper on PEP [21], which showed the conductivity of the bulk film structure with gaps wider than molecule length. In the previous paper, the device was fabricated by drop deposition and did not describe the device dimensions or the current density as it was difficult to measure the cross-section accurately. They simply showed the possibility that current flows through a very narrow path with a high current density, and is likely to be through a small number of molecules where random telegraph noise is observed. In the study presented here, the current flows through a single or a small number of PEP nanorods due to the fabrication process and the size of the CNT gap and the PEP molecule. The resistance of the CNT gap is estimated \(~\sim 10^{8}\) \(\Omega\). Note that the estimated resistance of the CNT–metal contact is \(~\sim 10^{5}\) \(\Omega\). This implies that the resistance of the CNT–metal contact cannot be dominant because it is much smaller than the other resistances due to the molecular wire or due to the tunnel barriers to the molecular wire. Therefore, these estimated resistances of CNT gaps should be dominated by the polymer molecules.

4. Conclusion

In summary, transport properties of PEP nanorods have been directly measured using SWNT electrodes. Rod-like PEP molecules were encapsulated with a side chain, forming inherently stable, individual, wire-like structures. A nanoscale gap was introduced onto individual SWNTs in a FET structure which was then bridged by PEP nanorods for electrical measurements. It was found that significant current can flow through individual or a small number of PEP molecules connected to SWNT electrodes. The current density of PEP nanorod was estimated to be in the range of \(~\sim 10^{5}–10^{6}\) A cm\(^{-2}\), showing that the PEP molecule has strong potential as a nanowire material.

References