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To cite this article: J Aprojanz et al 2017 J. Phys.: Condens. Matter 29 494002

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Amin M Saleem, Sareh Shafiee, Theodora Krasia-Christoforou et al. J. Phys.: Condens. Matter 29 (2017) 494002 (6pp)

https://doi.org/10.1088/1361-648X/aa9494

Highly anisotropic electric conductivity in PAN-based carbon nanofibers

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Received 23 August 2017, revised 17 October 2017 Accepted for publication 19 October 2017 Published 15 November 2017



Abstract

In addition to the chemical and physical properties of nanostructures their successful utilization for applications is strongly triggered by economic aspects. Electrospinning of nanowires from solution followed by subsequent annealing steps is a comparably cheap technique to fabricate conductive carbon nanofibers (CNF) made from polyacrylonitrile (PAN) molecules in large quantities. In this work, we investigated the microscopic properties of the CNFs with diameters of 100–300 nm by means of Raman and x-ray photoelectron spectroscopy and correlated these results with transport measurements done with a 4-tip STM. In particular, we investigated the effect of fiber alignment and knot densities, which can be controlled by applying constant creep due to stress during the stabilization process. The comparison of the conductivity obtained from single CNFs revealed further that the fiber crossings within the ensemble structure act as scattering centers and proofs that the transport is along the surfaces of the CNFs.

Keywords: carbon fibers, transport, 4-tip STM

(Some figures may appear in colour only in the online journal)

1. Introduction

The application range of carbon fibers is nowadays very diverse. Besides high stiffness and high tensile strength carbon fibers exhibit a large chemical resistance and low thermal expansion [1-3]. Therefore they are commonly used in lightweight construction or composite reinforcements. The good electric conductivity makes them promising materials for opto- and nanoelectronics [4]. Particularly for nm-sized CNFs, the high porosity and surface to volume ratio make such structures interesting for sensor applications as well as

for electrochemical capacitors and rechargeable lithium-ion batteries [5]. Moreover, the use of truly nm-scaled fibers may come along with an increased elasticity suitable for electromechanical applications [6, 7].

Usually, the preparation of carbon fibers follows similar schemes, but using different precursor molecules. The most often used precursor is polyacrylonitrile (PAN), which is used in 90% of commercially available carbon fibers. Alternative precursor materials are rayon or pitches. The fabrication of all carbon fibers comprises in general three subsequent steps, i.e. stabilization, carbonization and graphitization at different temperatures and annealing times [8]. Commercially available carbon fibers have an average diameter of around 10 μ m. This

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Figure 1. ((a), (b)) Top view SEM images of a CNF mats processed at 1500 °C without and with additional creep in the previous step, respectively. (c) Cross-sectional side view SEM image of the same mat as in (b). The inset depicts a zoom-in showing individual nanofibers. (d) Histogram of nanofibers with different diameters.

work adapts the conventional fabrication process to PANfibers made by electrospinning, resulting in average diameters around 100–300 nm.

Electrospinning is a powerful method to produce polymer fibers from various solutions with different diameters. Typically, a high voltage is applied to a polymer solution or melt while it is continuously pressed through a metal needle. The droplet formed at the metal tip is stabilized by the surface tension of the solution. However, due to the applied high voltage the drop is attracted by Coulomb forces from the collector. If these forces exceed the surface tension of the drop, it collapses and a so-called Taylor-cone forms [9]. This results in fibers being drawn to the collector. The fibers become thinner as the solvent evaporates and electrostatic forces generate stress because of the dynamic movement. The resulting fibers have a diameter which is between 50 nm and 10 μ m depending on polymer and spinning parameters [10]. Finally, the alignment of the fibers and their surface structure are strongly influenced by the subsequent annealing processes. In contrast to others, we have processed the CNFs with a constant creep due to stress and comparably low temperatures not exceeding 1700 °C.

The electric properties of these metallic CNF networks are governed by different effects. On a microscopic scale, band and hopping conductivity are a result of the carbonization and graphitization process [11]. On a macroscopic scale, however, percolation needs to be considered. Particularly, if the lengths of the CNFs are on average shorter than the device geometry, transport occurs only above the percolation threshold. For carbon nanotube wires it was shown that a critical angle for the misalignemnt of the nanotubes is indeed necessary to reveal a high conductivity along the fiber ensembles [12]. In this work we studied electrospun carbon nanofiber ensembles with high aspect ratios. We will show that our CNFs, produced with a considerably lower thermal budget, reveal extremely high conductivities along the wire direction. Moreover, we will show that the transport along the wires is hindered by the fiber crossings acting as scattering centers. This directly proofs, that the electron transport channels are close to the surface of the fibres, which is a prerequisite for any sensor application. From Raman and XPS measurements we conclude that graphitic crystallites are already formed with these temperatures. Most importantly, the anisotropy and conductivity can be increased by applying constant creep at 250 °C.

2. Experimental details

Polyacrylonitrile (PAN, 150.000 mw, Sigma-Aldrich) was used as starting material to prepare the carbon nanofibers via electrospinning. The polymer was dissolved in dimethylformamide (DMF, Carl Roth) with a concentration of 16 w%. In a typical electrospinning setup with a continuous solvent flow rate of 0.85 ml h^{-1} a voltage of 16 kV was applied to the solution with a fixed collector to needle distance of 18 cm. To obtain aligned fibers a rotating collector with a speed of 12 m s^{-1} was used. Oriented fibers were afterwards heated at 250 °C in air. To acquire the chemical cyclisation the samples were thermally treated and subjected to different mechanical loadings. In our experiments three load cases were considered. First, no load, which result in no product after heat treatment. Second, fixed fibers, (no elongation, no strain) mechanical stress only due to retardation (figure 1(a)). Third, fibers mechanical loaded with a weight as described in [13]



Figure 2. (a) Raman spectra recorded for different carbonization temperatures of 1300 °C, 1500 °C and 1700 °C. (b) Corresponding XPS spectra acquired on the same samples as in (a). (c) Intensity ratio of the D- and G-band from Raman (left scale) and sp^2 -fraction from XPS (right scale). (d) Relative intensity of the 2D-band (left scale) and A-band (right scale), which are characteristic for the crystalline and amorphous fraction in graphite, respectively.

which results in elongation of the fibers. This treatment also improves the alignment of the fibers. The applied stress in the order of 8 MPa results in an elongation up to 100%. The total heating time was 10h. The cyclized fiber mats were finally treated at reducing atmosphere (2% H₂ in Ar) for 10h. After an initial 0.5 h at 1100 °C the samples were heated up to 1300 °C, 1500 °C and 1700 °C, respectively.

The microstructure and morphology of as-electrospun nanofiber mats were characterized by a Gemini type scanning electron microscopy (SEM) with a primary electron acceleration voltage of 15 kV and an emission current of 1 nA. Insights about the crystallinity of the fiber mats were gained by Raman spectroscopy and x-ray photoelectron spectroscopy (XPS). All Raman spectra were acquired using a laser excitation wavelength of 532 nm and an incident power of 2.4 mW. The XPS experiments were performed using an Al-K $_{\alpha}$ emission while the kinetic energies were measured using a hemispherical analyzer with a pass energy of 20 eV. The transport properties were characterized by means of a 4-tip STM/SEM. The specific design of this microscope allows to perform transport measurements in different tip arrangements on scales ranging from mm down to nm. More details about transport measurements and the setup are reported elsewhere [14].

3. Results and discussion

3.1. SEM, Raman and XPS on carbon nanofiber ensemble structures

The morphology of the CNF ensembles fabricated by electrospinning was characterized by SEM. Figures 1(a) and (b) depict the top view of two nanofiber mats carbonized at 1500 °C without and with application of creep stress in the previous step, respectively. In both cases the mats are composed of smooth, continuous and almost defect-free fibers. Apparently, the alignment of the fibers is affected by the elongation induced by the creep due to stress applied during the stabilization process. Whereas the order of the fibers is not affected, the deviation angles of the fibers become smaller. The largescale cross-sectional SEM image figure 1(c) shows that the 80 μ m thick mats in our case were spun in a layer-by-layer fashion pointing towards a weak interconnection between the individual layers. The transport experiments presented below will support this. The average fiber diameter of ≈ 280 nm was determined from the statistical analysis of cross-sectional SEM images (figures 1(c) and (d)). Moreover, the inset of figure 1(c) reveals that some fibers are composed of even smaller wires with diameters less than 100 nm. In any case, the diameters of the fibers are determined by the electrospinning parameters and the elongation by the creep. In addition, we also analyzed the structures of CNFs carbonized at 1300 °C and 1700 °C. Within the error bars, both the alignment and diameter were quite similar to those shown for the 1500 °C samples.

Summarizing this part, the application of additional creep due to stress results in densely-packed and perfectly aligned nanofibers, while the diameters of the individual wires are almost unchanged. This opens the possibility to study the importance of percolation within these CNF ensemble structures.

Regarding the crystallinity and chemical composition of the fibers Raman and x-ray photoelectron spectroscopy measurements were performed. Figure 2(a) shows typical Raman spectra for various carbonization temperatures ranging from 1300 °C up to 1700 °C. The spectra were analyzed by using mixed Lorentzian-Gaussian functions. The entire spectrum could be accurately fitted including five bands. The peaks at 1600 cm⁻¹ and 1354 cm⁻¹ were attributed to the G- and



Figure 3. (a) Linear I-V curves obtained from rotational micro-square measurements for different angles in respect to the fiber axis. (b) The resistance measured as a function of the rotation angle for a fiber mat with (red) and without (black) additional creep. (c) 2pp and 4pp transport measurements on single CNFs and bundles of CNFs. The corresponding resistances as a function of the probe spacing are shown below.

D-band, which are related to ordered and defective graphitic crystallites, respectively [15]. The positions of these two bands are independent of the carbonization temperature. Additional bands at 1521–1535 cm⁻¹ (A), 2661–2686 cm⁻¹ (2D) and 2916–2936 cm⁻¹ (D + G) can be associated with amorphous carbons and second-order modes, respectively [15]. For all samples investigated here, the annealing of PAN-fibers after electrospinning results in the formation of graphite or graphene-like patches along the CNFs.

The crystallinity of the CNFs can be quantified further by analyzing the Raman intensities. The R-value, i.e. the I(D)/I(G)-intensity ratio, depends on the concentration of defects including grain boundaries and graphite edge planes as well as on the alignment of the graphitic planes and the degree of graphitization [16]. Figure 2(c) shows that the R-value decreases from 2.3 to 1.4 strongly indicating an ongoing transformation of amorphous into crystalline graphite or multilayer graphene with increasing carbonization temperature. This finding is in complete agreement with the decreasing I(A)/I(G) and increasing I(2D)/I(G) ratios (see figure 2(d)). To determine the crystallite domain size L_a an empirical formula $L_a(nm) = 4.4/R$ was developed by Knight and White [17]. From this equation, L_a was enlarged by 64% from 1.91 to 3.14 nm.

Additionally, XPS studies were performed on the same CNF mats. Figure 2(b) depicts representative C1s-spectra of these mats. The spectra were deconvoluted into three major contributions attributed to the so-called shake-up emission at 290.7 eV, sp²-hybridized carbons at 284.4 eV and sp³-hybridized carbons at 285.2 eV [18, 19]. We should point out that we did not detect any N-based emission or contaminations, i.e. the carbonization of the PAN fibers took fully place in a clean environment. The influence of the carbonization temperature on the crystallinity of the mats was analyzed by comparing the peak area of the sp²-carbons in respect of the sp³ peak area. Figure 2(c) shows that the contribution to the C1s spectrum of sp²-hybridized carbons increases from 54% up to 63% with increasing temperatures. This correlates perfectly with the Raman results proving the conversion of disordered carbonaceous components into ordered graphite.

Graphitization temperatures of around 1700 °C are obviously high enough to reduce the amorphous fraction down to $\approx 10\%$ as deduced from the decrease of the amorphous fraction with respect to the G-band. The information depth of Raman is comparable with the diameter of the CNFs, i.e. also the core of the fibers crystallizes at these temperatures. Contrary, XPS is way more surface sensitive and the mean free path length is around 10 monolayers. This clearly shows that indeed the surfaces of the CNFs consists of graphite or multilayer graphene. Due to experimental restrictions we could not anneal the fibers to higher temperatures in order to check if the R-value could be lowered further or if the spatial constrictions in the center of the fiber suppresses in general the growth of long range ordered surfaces. Despite these residual defects, the fibers showed an extremely good electric conductivity, as we will show in the following.

3.2. Electric transport properties

In order to study the anisotropy and effects of cross-links within the CNF mats we performed transport measurements using a 4pp square configuration, which reliably allows to determine the conductivity components parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the fiber axis. The resistances were calculated from the slope of the I-V-curves recorded for various angles with respect to the preferential orientation direction. The linearity of the IV-curves is a hallmark for an Ohmic behavior (see figure 3(a)). The measured resistances are plotted in figure 3(b) both for CNFs treated with elongation due to creep stress (red circles) and without (black circles) elongation but mechanical stress due to retardation. As obvious, both data sets R_{Θ} are well described by the so-called rotational square micro-4PP equation [20]:

$$R_{\Theta} = \frac{1}{2\pi\sqrt{\sigma_{\parallel}\sigma_{\perp}}} \times \ln \sqrt{\frac{\left(\sigma_{\parallel}/\sigma_{\perp}+1\right)^2 - 4\cos^2\Theta\sin^2\Theta\left(\sigma_{\parallel}/\sigma_{\perp}-1\right)^2}{\left(\sin^2\Theta + \sigma_{\parallel}/\sigma_{\perp}\cos^2\Theta\right)^2}}$$

depending on the conductivities parallel σ_{\parallel} and perpendicular σ_{\perp} to the fibers as well as on the anisotropy ratio $\sigma_{\parallel}/\sigma_{\perp}$. According to this model, the conductivity along the fibers increases from around 220 mS/ \square to 420 mS/ \square while the values across the axis (transverse direction) decrease from approximately 20 mS/ \Box down to 10 mS/ \Box , if creep was applied during the stabilization process. The fiber mat processed with elongation due to stress shows an almost 4 times larger anisotropy. To the best of our knowledge, this value is the highest anisotropy ratio reported so far for PAN based nanofiber ensembles. Please note, the formula mentioned above is strictly valid only for anisotropic 2D electron gas systems. Obviously, the coupling in between the individual CNF layers is even lower compared to the in-plane perpendicular direction, which is most likely the result of the spinning process. Therefore, the individual CNFs represent weakly interacting 1D conductors, in agreement with our structural findings discussed in context of figure 1. Most importantly, the cross-connections between the fibers cause electron scattering, thus reducing the conductivity along the wires. This shows, that the electronic transport is mainly along the surfaces of the individual CNFs.

In order to support this conclusion we measured the transport along single CNFs, which were fabricated simply by rubbing the CNF base material onto an oxidized, i.e. insulating Si-surface for subsequent transport measurements. According to the cross-sectional SEM images (see figure 1(c)) also bundles of CNFs were isolated from the ensembles. Three characteristic individual fiber classes are shown in figure 3(c). In addition, these SEM images also show the STM tips brought into contact with the fibers. For a single CNF with a typical diameter of 130 nm we measured a resistivity of 14 k $\Omega \mu m^{-1}$. The probe distance dependent measurements extrapolate to zero, i.e. the contact resistance is negligible for the 2pp measurements. This is in accordance with the 4pp measurement, which was used for the so-called loose bundle scenario. SEM images show that these bundle structure consists of smaller CNFs, which touch each other only pointwise. The resistance per length across this bundle scenario is quite similar. In contrast, for densely packed bundle structures, where the current can be applied more easily to all of these, the overall 1d resistivity is lower by one order of magnitude. The apparent diameter of the dense bundle structure is around 1 μ m, thus the resistivity is approximately 7 times smaller. Measurements on single fibers from differently treated mats, e.g. with and without applying creep, revealed almost similar resistance values, thus the anisotropy mentioned above is rather due to the alignment of the fibers than due to a different graphitization of the fibers.

This reasonable scaling behavior supports our initial finding that the individual CNF has a 1D resistivity of around 14 k Ω μ m⁻¹, which refers to a bulk resistivity of 190 $\Omega \mu m$, $(\rho_{SF} = R/L \cdot A = R/L \cdot \pi \cdot r^2)$. This value is in reasonable agreement with previous studies on single fibers made from PEDOT precurser molecules [21]. From this we can estimate the mean free path lengths via
$$\begin{split} \lambda &= v_{\rm F} \cdot \tau = v_{\rm F} \cdot \frac{m^*}{e^2 n \rho_{\rm SF}}. \mbox{ Using values for bulk graphite} \\ (m^* &= 0.004 m_e; v_{\rm F} = 0.94 \cdot 10^6 \mbox{ m s}^{-1}; n = 3 \cdot 10^{18} \mbox{ cm}^{-3} \mbox{,} \end{split}$$
[22]) we finally obtain a mean free path length of $\lambda \approx 2.4$ nm, which is in reasonable agreement with the values deduced from Raman (see above). Accordingly, for the tight bundle shown in figure 3(c) a bulk resistivity of around 550 $\Omega\mu$ m was calculated assuming a height and width of 200 nm and 1 μ m, respectively, measured by STM (not shown) and SEM. The increased 3d-resistivity for the tight bundle underlines once more our finding that the transport is mediated by the surfaces of the fibers.

To summarize our results, the graphitization of nm-sized CNFs based on PAN with creep due to stress results in highly conductive and structurally defined fiber ensembles. Based on XPS, Raman and *in situ* 4pp-STM/SEM transport we showed that the surface near areas are reminiscent of multilayer graphene structures. This causes the high carrier mobilities along the fibers and close to their surfaces. Moreover, we showed that any disorder along the wires, e.g. formation of cross-links, severely reduce the transport properties. Therefore, both the control of ordering on microscopic and macroscopic length scales is the key parameter for any fabrication of light-weight conductors.

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) and the Hannover School for Nanotechnology (hsn) within the Lower Saxony PhD-program.

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