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2002 J. Phys.: Condens. Matter 14 11125

(http://iopscience.iop.org/0953-8984/14/44/437)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11125–11129 PII: S0953-8984(02)38610-7

Resistivity and fractal structure in carbon nanotube networks

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Received 24 June 2002
Published 25 October 2002
Online at stacks.iop.org/JPhysCM/14/11125

Abstract

We have measured the temperature and magnetic field dependence of the resistance for bulk samples of single-walled nanotubes treated in different ways. Hydrostatic pressure-treated samples and as-grown samples show a two-dimensional variable-range hopping behaviour while samples treated in non-hydrostatic pressure or in acid for a long time show a three-dimensional transport behaviour. We suggest that the observed two-dimensional behaviour arises from a network structure with a fractal dimension lower than three.

1. Introduction

Single-walled carbon nanotubes (SWNTs) are of great interest, both as a test-bed for new ideas in physics and from the point of view of potential applications. As-grown SWNTs form bulk networks (mats), in which tubes are bundled together in 'ropes' and which also have unique structures and properties [1]. Many transport studies have been carried out on such mats, but the results differ from sample to sample and it is not clear which properties are intrinsic to nanotubes. Many recent experiments suggest a variable-range hopping (VRH) mechanism below room temperature [2–9]. Because a SWNT mat is a three-dimensional (3D) array of 1D linear molecules, a 3D VRH mechanism is expected from simple arguments. Surprisingly, however, experiments on some samples show instead a clear 2D VRH behaviour [3, 8]. In this report we show that there is a correlation between the mesoscopic structure of the sample and the observed dimensionality structure of the conduction mechanism, and we give a tentative explanation in terms of the fractal dimensions of the dominant conduction paths.

2. Experimental details

The samples used were synthesized by arcing metal-oxide-impregnated graphite rods as described elsewhere, using Ce and Ni as catalysts [9]. As-grown mats were collected around the graphite cathode. SEM images and Raman spectra showed that as-grown mats are formed

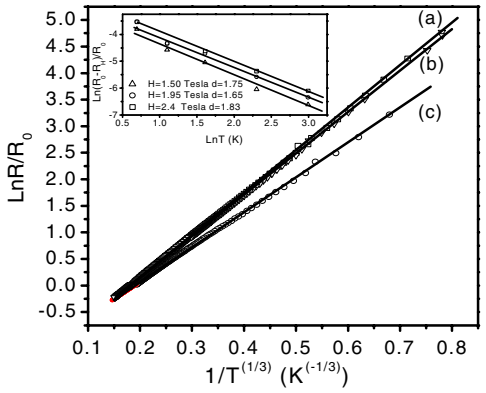

Figure 1. ln R for (a) as-grown mats, (b) a mat treated in acid for 0.5 h and (c) a mat treated under 1.5 GPa hydrostatic pressure for 3 h, plotted as a function of $T^{-1/3}$. The inset shows $\ln[(R_H - R_0)/R_0]$ versus ln T at a fixed magnetic field.

as a continuous network of entangled single-walled nanotube bundles, 10–30 nm in diameter and with an average length between entangled points of 100 nm. Some regions contained mainly long, large-diameter bundles and only few amorphous carbon particles, while other regions had a lower density of smaller bundles and some amorphous carbon particles [9].

Samples were treated in different ways to create different microstructures and morphologies. Some mats were treated under hydrostatic pressure at 1.5 GPa for 3 h, using a 50/50 mixture of iso-/*n*-pentane as a pressure medium and a denser sample composed of several small pieces of as-grown mat were pressurized without any pressure medium at 0.3 GPa. Hydrostatic pressure should improve inter-tube contacts while non-hydrostatic pressurization should give a denser sample but damage tubes and change the intrinsic morphology of the network. Other mats were treated in concentrated nitric acid for 0.5–2 h, washed with distilled water and annealed at 1000 °C in flowing Ar gas for 1 h to remove residual oxides. The treated samples were cut into pieces $5 \times 1 \times 0.2\,\mathrm{mm}^3$ and silver paint or pressure contacts were applied in a four-probe configuration. The dependence on temperature (T) of the resistance (R) in the range 2–300 K and the magnetoresistance (MR) up to 5 T were measured in an Oxford 2000 variable-temperature cryogenic system using current smaller than 20 μA.

3. Results and discussion

Depending on the initial treatment of the samples, their transport properties showed either a 2D or a 3D conduction behaviour. Typical results for samples treated under 'gentle' conditions, i.e. samples consisting of as-grown mats, either treated under hydrostatic pressure or treated for a short time in acid, are shown in figure 1. Figure 1 shows the electric resistance in the range 2–300 K for three samples, plotted as ln R versus $T^{-1/3}$. For an as-grown mat, the resistivity decreased with increasing T, showing a 'semiconducting' behaviour. The data for this sample form a straight line in figure 1(a), indicating that $R(T)$ obeys the equation

$$R(T) = R_0 \exp(T_0/T)^{1/\beta}, \tag{1}$$

valid for VRH [10], with $\beta = 3$. Here $T_0 \sim 13.8/\kappa_B g(E_F)\xi^d$, where ξ is the localization length, $g(E_F)$ is the density of states at Fermi level and d is the dimensionality of the system. The exponent $\beta = (1 + d)$, indicating that for this sample we have 2D VRH, in spite of its 3D physical structure. The measured slopes were almost the same for several samples, giving a T_0 of approximately 525 K. We stress that no reasonable fits to the data could be made for β-values of 2 or 4 in equation (1).

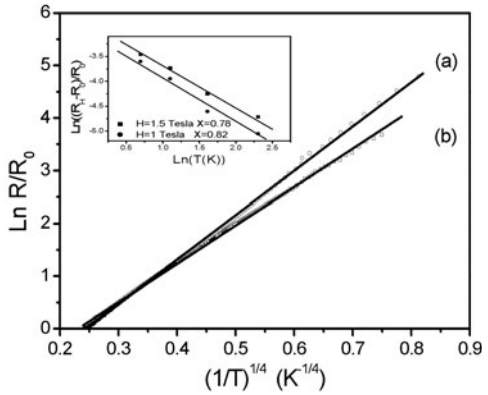

Figure 2. ln R for (a) a mat treated in acid for 2 h and (b) a sample consisting of several pieces compressed under non-hydrostatic pressure of 0.3 GPa, plotted as a function of $T^{-1/4}$. The inset shows $\ln[(R_H - R_0)/R_0]$ versus $\ln T$ at a fixed magnetic field.

For samples purified in nitric acid for 0.5 h, Raman and SEM studies showed a definite decrease in the number of nanoparticles with no obvious change in the morphology of the tubes. Figure 1(b) shows that the resistance of such a 'high-purity' sample follows the same behaviour as the as-grown mat with only a small decrease in T_0 to 485 K.

We show data for the resistance of a sample pressurized hydrostatically at 1.5 GPa for 3 h in figure 1(c). Pressurization permanently decreased the thickness of the mat, indicating that the inter-bundle contacts are probably improved. Again, the data points form a straight line in the figure but now with $T_0 = 287$ K, significantly smaller than the original value. Compaction should indeed induce an overlap of electron wavefunctions, resulting in an increase of localization length and thus a decrease in T_0.

The dimensionality of the conduction mechanism can also be estimated from data for the MR, We measured MR data from 2 to 10 K for an as-grown sample. At low fields electron interference gives a negative MR, while high fields contract the wavefunction, destroy the phase coherence and hence reduce the hopping probability, giving a positive MR [10]. In the low-field range, the negative MR is predicted to have a T-dependence:

$$\Delta R_H = [R(T, H) - R(T, 0)]/R(T, 0) = -AH^{\alpha}T^{-x} \tag{2}$$

where $x = 3/(d+1)$ and α is 1 or 2 [10]. Data for $\ln \Delta R_H$, extracted from MR data, are shown as a function of $\ln T$ in the inset of figure 1. From the slope we find $d \approx 1.7$, very close to 2, verifying that 2D VRH is indeed the dominant transport mechanism in the as-grown mat.

Samples treated under more severe conditions, such as compression under non-hydrostatic conditions or immersion in acid for a long time (2 h), showed a different behaviour. This is illustrated in figure 2, where we plotted $\ln R$ for two samples as functions of $T^{-1/4}$. The data again fall on straight lines, indicating that for these samples the electrical transport obeys Mott's VRH mechanism in 3D. From the slopes we find $T_0 = 4950$ K for the acid-treated sample and 3100 K for the compressed one. Again, we stress the fact that in these cases good fits could not be obtained for $\ln R$ versus $T^{-1/3}$ or $T^{-1/2}$. Measurements of the MR showed the same general tendency as before, and plotting $\ln \Delta R_H$ as a function of $\ln T$ (the inset in figure 2) we find $d \approx 2.8$, very close to the 3D indicated by the results for $R(T)$. For both groups of samples we thus obtain consistent results, but with different dimensionalities. This result is also consistent with most literature data: either 2D VRH or 3D VRH was found in different samples [3, 4, 6].

To understand why initially identical samples treated in different ways behave in such radically different ways, we need to know how their structures have been modified by the treatment. The mats treated by acid for a long time were very pure, with hardly any metallic

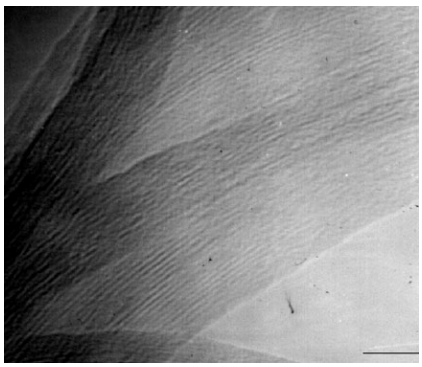

Figure 3. A HRTEM image for an as-grown mat with fine branches. The unit bar is 12.5 nm.

or amorphous carbon impurities. However, their morphology had changed significantly. The bundles became much more strongly curved than before [9]. Acid treatment is expected to remove amorphous carbon and metals, but also damaged nanotubes and tubes with defects, and even a certain fraction of 'perfect' tubes. It is likely that single tubes or very thin bundles branching out from thicker bundles are more likely to react with the acid than tubes in thicker bundles. The finer links in the continuous network observed initially therefore break up. The initial randomly multiply connected network is therefore transformed by acid treatment into an apparently more 'regular' quasi-lattice of denser regions, connected by relatively few nanotube bundles. The sample consisting of several pieces of mat, pressed together under non-hydrostatic conditions, should have a similar structure but on a larger scale. Generalizing, for the sake of the argument, 3D VRH is thus observed in materials consisting of denser regions linked by relatively few conducting paths and 2D VRH in materials containing a large number of randomly connected conducting paths.

To explain our results, we argue that the apparent 2D VRH arises from a fractal structure of the conducting paths in as-grown materials. In the formation of these samples, tubes branch out randomly from bundles and reconnect to form a finely branched, multiply connected network which, in analogy with the branches of trees etc, should have an effective geometrical dimension smaller than three; the experimental results indicated $d \approx 2$. Figure 3 shows a high-resolution TEM (Hitachi-8100) image for an as-grown mat with fine branches. This fractal structure is probably strongly modified during purification by acid treatment or oxidation in air, which preferentially breaks up the finer links. The treatment thus leaves a final network which is more truly three dimensional with far fewer and more regular interconnections, linking mainly neighbouring denser regions. Such an explanation agrees with available structural and transport data for our carbon nanotubes. Fractal conducting networks are also observed in many morphologically similar materials, for example conducting polymer composites consisting of an insulating matrix containing a conducting phase such as carbon black, metal powder or wires, or conducting polymer such as polyaniline (PANI). The fractal nature of the structure has important effects on the electrical transport properties of these materials. As one example, for conducting (doped) PANI in a poly(methylmethacrylate) (PMMA) matrix [11], measurements indicate that electrical transport occurs through VRH with an exponent β which varies continuously from 4 for pure PANI, indicating 3D hopping, over 3 (2D hopping), to 2 (1D hopping) at about 10% PANI. The apparent dimensionality thus changes continuously with the structure of this system as more branches form (or disappear). It seems reasonable to assume that a similar effect may occur if we replace the multiply connected fibril-shaped PANI network by a topologically similar nanotube network.

To summarize, we find that pressure and acid treatment change the transport properties of as-grown nanotube networks significantly, from an initial apparently two-dimensional VRH mechanism to three-dimensional VRH. Structural studies lead us to suggest that this change is caused by a break-up of an initial multiply connected random structure with a fractal dimension near two to a regular, three-dimensional structure, as also observed in composite conducting materials.

Acknowledgments

This work was financially supported by the Swedish Research Councils for the Natural (NFR) and Engineering Sciences (TFR), by the Scientific Research Foundation for Returned Overseas Chinese Scholars (no 2001-498), by the Natural Science Foundation of China (no 10144004) and by the Nanometre Material Project and Project for Young Teachers of Jilin University.

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