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Localization in single-walled carbon nanotubes

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Abstract

We demonstrate that in low temperature semiconductor-like regions the electrical resistance of single-walled carbon nanotube mats is highly nonlinear with a temperature-dependent threshold field for the onset of nonohmic conduction. The modest applied electric field completely suppresses the upturn in resistance and recovers metallic behavior over the entire temperature range 2.2 K $< T <$ 300 K. The transport data indicate low-temperature localization of charge carriers arise from disorder on the nanotube bundles themselves and not from granularity casued by weak interbundle connections. The temperature-independent localization radius a is determined to be approximately 330 nm. © 1998 Published by Elsevier Science Ltd.

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Single-walled carbon nanotubes (SWNTs) constitute an intriguing physical system. Individual achiral (n,n) SWNTs are predicted to be metallic nanowires [1–3] with angstrom-scale diameters. As such, SWNTs provide a model system for studying the electronic properties of one dimensional materials. Macroscopic quantities of SWNTs have been synthesized by a variety of catalyst-assisted techniques [4–7]. Remarkably, many bulk samples of SWNTs consist largely of bundles [6], containing from a few to hundreds of parallel single-walled tubes arranged in a triangular lattice. X-ray diffractometry of both laser ablation and arc-discharge synthesized SWNTs shows a narrow diameter distribution for tubes within the bundles, peaked around that of the metallic (10,10) tube [6,7].

Resistance measurements of individual SWNT bundles as well as macrosopic mats of SWNT indeed show metallic electrical resistance at high temperatures (i.e. increasing resistance with increasing temperature), but at low temperatures the resistance shows a semiconductor-like upturn [8], rising slowly with decreasing temperatures. A crossover from metallic to nonmetallic behavior is not unexpected in low-dimensional systems, as these systems are particularly unstable to charge- or spin-density wave formation, and localization is predicted to occur in one dimension regardless of the degree of disorder. Other possible explanations for the resistance upturn include localization by strong defects on the tubes or bundles themselves, weak connections between bundles, or even the presence of small amounts of magnetic impurities causing a Kondo effect.

In this article we present measurements of the absolute electrical resistance R of bulk SWNT samples as a function of the electric field E and temperature. In the low temperature semiconductor-like regime, R is found to be highly nonlinear beyond

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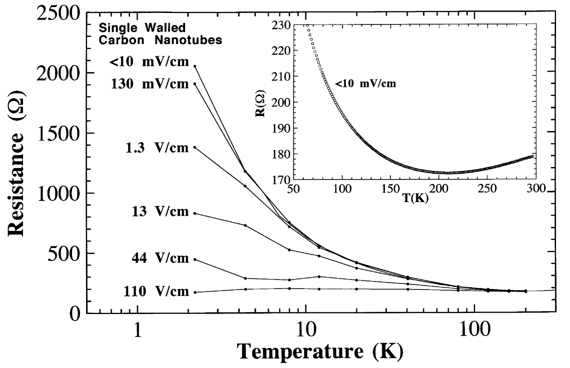

Fig. 1. The electrical resistance of an SWNT mat is shown as a function of temperature for various values of applied electric fields. The inset shows the ohmic resistance of the same sample in the high temperature region.

a temperature-dependent critical threshold field E_c. At modest values of E, the low-temperature conductance is significantly enhanced and metallic behavior is recovered for the entire measured temperature range $2.2\ K < T < 300\ K$. We interpret the low-field resistance upturn as arising from on-bundle strong

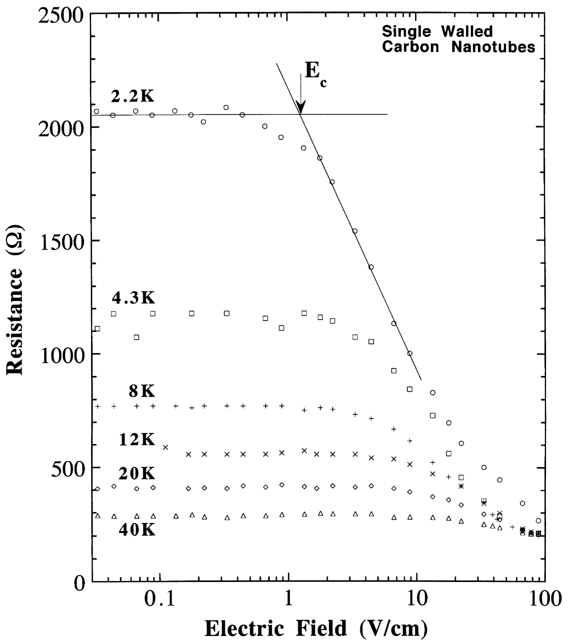

Fig. 2. The resistance of an SWNT mat is plotted as a function of applied electric field at temperatures 2.2, 4.3, 8, 12, 20 and 40 K. The definition of E_C is discussed in the text.

defect-induced localization of carriers. The localization radius a is explicitly determined.

SWNT samples used in this study were synthesized by both laser vaporization [6] and arc-discharge methods [5,7] with similar results. The samples consist of mats of purified SWNT bundles. Electrical contact to the samples was made using conducting silver paint in a standard four-probe configuration. Resistance as a function of temperature was first measured at a low electric field (the ohmic regime) using dc and ac methods. The electric field dependence of the resistance was then measured at various fixed temperatures. A standard time-resolved pulsed ($\leq$ 10 μs) current technique was employed to measure the resistance: the current drive and voltage response pulses were displayed simultaneously on an oscilloscope, allowing for time resolution of the resistance during the pulse and separation of the effects of (time-dependent) sample self-heating from intrinsic nonlinearities. Samples with room temperature resistances ranging from 100 to 2000 Ω were measured with similar results. All data shown in this communication are from a single representative sample.

Fig. 1 shows the resistance versus temperature $R(T)$ of an SWN mat at various applied electric fields. As shown in the inset, the low electric field (ohmic) resistance is metallic near room temperature, displays a minimum near 200 K., and rises below. The main body of Fig. 1 shows the resistance at selected electric fields. At low temperatures a large change in R with electric field is evident even at modest electric fields. At the highest measured fields, the resistance upturn disappears and $R(T)$ is essentially temperature-independent at low temperatures within our experimental resolution.

Fig. 2 shows the detailed electric field dependence of the resistance in the low-temperature nonlinear regime. Different $R(E)$ data sets were collected at fixed temperatures, as indicated. At low E, ohmic (i.e. field-independent) resistance is observed, while beyond a critical threshold electric field E_c the resistance decreases with increasing E. The field-independence of the low-field approximately three orders of magnitude lower than that indicated in the figure. Fig. 2 shows that the critical threshold field E_c is temperature-dependent, decreasing with decreasing temperature. Because the scatter in the $R(E)$ data makes it difficult to extract E_c from a conventional derivative

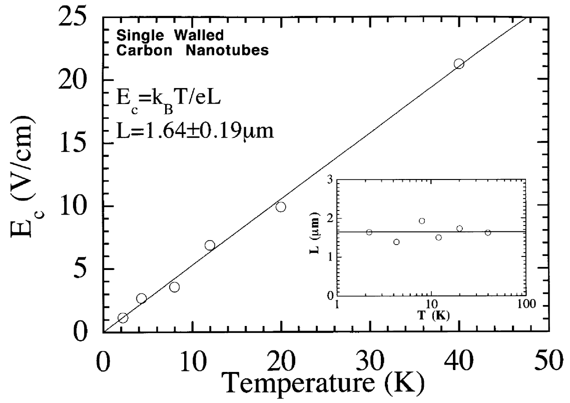

Fig. 3. The critical electric fields, E_C, shown in Fig. 2, is plotted as a function of temperature. The inset shows the localization length scale L, defined in the text, as a function of temperature. The line denotes the average value, 1.64 μm.

plot we define E_c as the intersection of extrapolated fits to the low-field ohmic and initial nonlinear conduction regimes, as discussed later and indicated on the $T = 2.2$ K data of Fig. 2.

Nonlinear resistance with a threshold field indicates unusual nonmetallic conduction. Possible nonlinear conduction mechanisms for SWNTs include sliding charge or spin density waves, field-induced donor ionization (Frenkel–Poole effect) and avalanche breakdown (Zener effect) in semiconductors and weak or strong charge localization owing to impurities and defects. We rule out semiconducting behavior as the source of the nonlinearity because of the lack of activated behavior in the temperature-dependent low-field resistance. Dynamic charge- or spin-density waves are similarly discounted by the absence of activated behavior, the temperature dependence of E_c, and the lack of a frequency-dependent conductivity [9] in the microwave region. It is then likely that the nonlinearity we observe in SWNTs is because of carrier localization.

The effects of localization are generally reduced both by increasing the temperature and by increasing the electric field. Any system of localized charge carriers typically displays a characteristic electric field at which nonlinear conductivity begins to appear. We may equate the thermal energy k_BT with the electrical energy eE_cL at the characteristic field E_c in order to determine a length scale

$$L = k_BT/eE_c \quad (1)$$

of the localized system. In the case of localization of carriers as a result of granularity, L corresponds to the size of the metallic grains [10]; eEL is the energy gained by a carrier hopping from one grain to the next. In the case of localization of carriers as a result of strong disorder, L is qualitatively a measure of the Bohr radius a of a localized state; quantitatively $L \approx 5a$ [11].

To extract E_c from the data of Fig. 2, we adopt a simple curve fitting algorithm. Phenomenologically, above the critical threshold electric field the resistance of our SWNT samples drops approximately as

$$R = R_o(1 - S\ln(E/E_o)), \quad (2)$$

where R_o is the low-field (ohmic) resistance, E_o is an arbitrary constant, and S is the logarithmic slope. S is found to be roughly temperature independent. Extrapolation of the logarithmic portion of the $R(E)$ curves to the value $R = R_o$ gives a systematic and objective method of determining the critical threshold electric field E_c.

In Fig. 3 we plot E_c as a function of the temperature T. E_c is proportional to T over the temperature range studied, suggesting a temperature-independent length. We use Eq. (1) to extract L from E_c at each temperature. The inset of Fig. 3 shows L, thus determined, as a function of T; L is nearly temperature-independent at $L = 1.64 \pm 0.19$ μm. A different criterion for E_c, such as a specific percentage change in the resistance, gives similar results for L.

Together with other evidence, our determined length scale L can be used to distinguish which localization mechanism applies in SWNT samples. If the localization is because of granular metal effects, i.e. insulating connections between strands which are metallic, then L should be a measure of the strand length parallel to the electric field; voltage drops will be concentrated at the gaps between strands in each percolation path, with each drop having the magnitude EL, where L is the strand length. Thus a carrier would gain an energy eEL when hopping from one strand to another. The actual nanotube bundles in our SWNT samples are observed by transmission electron microscopy to be tens of microns in length, much longer than our observed localization length. Further, granular metal conductors are expected to have a highly frequency-dependent conductivity [12], with effects typically observable at frequencies as low as 10^2 Hz. A recent report [9] on the microwave conductivity of SWNT mat samples finds no frequency dependence of the conductivity to 10^{10} Hz. The authors of this study similarly ruled out granular metal effects as the cause of the low temperature resistance upturn in SWNTs. We thus conclude that the localization we observe is intrinsic to the individual SWNT bundles, and not a consequence of conduction across poor interbundle connections within the mat sample.

We suggest instead that the carriers in an SWNT bundle are in fact localized by disorder caused by intertube or intratube defects of deformations. The localization length scale L then determines the localization radius $a \approx L/5 \approx 330$ nm. The metallic nature of the (n,n) nanotube rests upon a $\pi - \pi^*$ symmetry which allows these bands to cross at the Fermi point. Any perturbation which destroys the symmetry lifts this degeneracy: the undoped (n,n) carbon nanotubes are very sensitive to environmental disturbances which can suppress or destroy the metallic density of states near the Fermi energy. Twisting an individual nominally metallic nanotube along its length induces a gap at the Fermi surface [13]. Coherent intertube interactions also break the symmetry and create a pseudogap at the Fermi energy, a suppression in the density of states which favors localization [14]. The low density of state in the $\pi - \pi^*$ plateau implies a pronounced sensitivity to doping which could be realized by material inhomogeneities such as residual metallic particles. Bond rotation defects also strongly perturb the electronic structure [15]. Finally, the introduction of a single pentagon–heptagon defect into a tube causes an abrupt change of wrapping indices, creating a semiconductor–semiconductor, metal–semiconductor or metal–metal junction which may greatly influence the transport properties [16–18]. It was recently observed experimentally that the electronic properties of SWNT bundles vary along their length, suggesting that defects in the bundles are indeed acting as electronic devices [19]. This class of defects would have a strong localizing effect on the carriers. The length scale for localization would then depend on the average separation between defects, and thus be temperature independent, in agreement with the results obtained here (Fig. 3).

The temperatures during nanotube growth vary from $\backsim$ 3000–4000 K during initial vaporization of the graphite precursor to $\backsim$ 1200 K in regions far removed from the arc discharge or laser focus. As the defects could form at any point during the synthesis, we consider the thermodynamic equilibrium defect concentrations at both 1200 and 3000–4000 K. Single pentagon–heptagon defects cost roughly half the energy of bond rotation, implying an equilibrium defect density of roughly 10^{-3} per atom, or one defect every $\backsim$ 10 nm along the (10,10) tube length at 3000–4000 K. The defect concentrations at $\backsim$ 1200 K are much ($\backsim$ 10^6X) lower. However, tube growth is in nonequilibrium and the single pentagon–heptagon defects are particularly difficult to anneal out after formation (they can anneal out only by annihilation with oppositely directed defects or migration to a tube edge). Therefore the defect concentrations for growth at 1200 K may significantly exceed thermodynamic estimates.

We find metallic behavior of the resistance of SWNT for temperatures 2.2–300 K at modest electric fields. We conclude that SWNT are intrinsically metallic, but at low temperatures and electric fields the charge carriers are localized by strong disorder, bringing about an insulating state. The onset of nonlinear conduction gives an estimate of the Bohr radius of the localized states a 330 nm. The short localization length and the lack of reported frequency dependence of the resistance up to 10 GHz indicate that poor interbundle junctions are not the source of the disorder. A likely source of the disorder is imperfections in the individual SWNT, which, given the high temperature during formation of SWNT, could be present in sufficient numbers to explain the magnitude of the localization length. Twists in the individual SWNT as well as intertube and interbundle interactions should also strongly perturb the metallic state.

Acknowledgements

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