Super-small energy gaps of single-walled carbon nanotube strands

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The temperature dependence of the resistance measured on long single-walled carbon nanotube (SWNT) strands has been investigated. By applying a simple model to the detailed analysis of our experimental results, we discovered a super-small energy gap of 1–3 meV, which is an intrinsic property of the "metallic" SWNT bundles in long SWNT strands. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1927269]

Materials can be classified as metals, semimetals, semiconductors, or insulators based on their electron energy bands. In the bulk electronic structure of a semimetal, there is only a very small overlap between the valence and the conduction bands, such as in graphite (40 meV)[1] or bismuth (38 meV).[2] This causes a semimetal to be a poor metal, on the verge of being a semiconductor with a band gap. Only a small change in the coordination of the lattice atoms (for instance, dimensional shrinking or element doping) is needed to disturb this delicate balance such that a semimetal could either turn into a better metal or into a semiconductor.[1,2] It has been predicted theoretically and confirmed experimentally that nanoscale graphite—carbon nanotubes—could be either metallic or semiconducting, depending on their assembled lattice configurations.[3–7] However, recent theoretical and experimental work has revealed that metallic single-walled carbon nanotubes (SWNTs) in a bundle form will open up a small energy gap or pseudo-gap (~0.1 eV) owing to intertube interactions in the bundle.[8,9] Detailed investigation indicated that intertube coupling in a bundle of librating nanotubes causes an additional band dispersion of ≈0.2 eV and opens up a pseudo-gap of the same magnitude at Fermi level.[10]

Theoretical calculations predicted that metallic nanotubes interact with each other in a bundle so as to open up a pseudo-gap in the Brillouin zone and modify the density of states (DOS) of the bundle near the Fermi energy.[8,10] The existence of the pseudo-gaps in the bundle makes the conductivity and other transport properties significantly different from those of isolated tubes. The experimentally observed small energy gaps (30–80 meV) depend inversely on the square of the tube diameter in zigzag metallic SWNT bundles, as do the small pseudo-gaps (80–100 meV) in bundles of armchair SWNTs,[9] suggesting that most metallic SWNTs are not true metals. Their electron transport properties would be different from that of conventional metals and also different from that of semiconductors. For chiral metallic SWNTs, the predicted gaps decrease rapidly with increasing index angles.[11] However, the gap magnitudes were poorly resolved due to computation limitation. By applying a simple model to the detailed analysis of our experimental results in this letter, we discovered a super-small energy gap (1–3 meV) in long chiral SWNT strands, based on both experimental and theoretical evidence of the temperature dependence of the resistance R (T) measured on long SWNT strands. We believe that this result represents an important step toward a deeper understanding of the electronic properties of carbon nanotubes and other one-dimensional nanomaterials.

Structurally rigid and highly conducting long SWNT strands used in this study [Figs. 1(a) and 1(b)] were synthesized by a vertical chemical vapor deposition method.[12] The centimeter long SWNT strands are large collections of well-aligned SWNT bundles, which consist of well-arranged SWNTs in a two-dimensional triangular lattice. The diameter of the SWNTs varies from 1.1 to 1.7 nm but was dominated by 1.1 nm tubes. In addition to the 1.1 nm diameter metallic chiral SWNT (11, 5), a metallic armchair SWNT (9, 9) and a semiconducting SWNT (21, 1) were also present in the long ordered SWNT strands based on our Raman investigation results.[12,13] The strands consist of thousands of SWNT nanotubes held together by van der Waals forces with a thickness of ~400 μm and were cut into a 1 cm length for electrical resistance measurements.

The electrical resistance was measured with a Quantum Design Physical Property Measurement System (PPMS) using the standard four-probe alternating current (ac) technique at 27 Hz with currents I of 0.01 mA and 1 mA separately.

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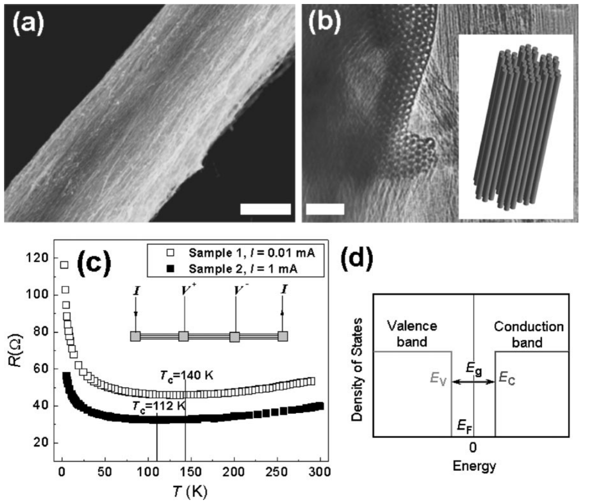

FIG. 1. (a) (Color online) scanning electron microscope image of a long SWNT strand, showing that aligned SWNTs extend continuously from one end of the strand to the other. Scale bar is 5 μm. (b) A cross-sectional view and a geometric model of a SWNT bundle consisting of a well-arranged two-dimensional triangular lattice. Scale bar is 5 nm. (c) Raw resistance temperature data of two long SWNT strands with different currents *I*. The crossover temperature T_c (from metallic to semiconducting) in Sample 1 (treated) and sample 2 (as-synthesized) occur at 140 K and 112 K, respectively. The inset shows a schematic diagram of resistance measurement. (d) The DOS of the 1D metallic SWNT near the energy gap is depicted as the solid line, where E_v and E_c are the edges of the valence and conduction bands, respectively. The units here are arbitrary.

Two types of samples were investigated and the typical results are shown in Fig. 1(c). Sample 1 was first dipped in HCl acid for 8 h and then annealed under an argon atmosphere at 1800 °C for 2 h to remove catalyst impurities and a very small amount of amorphous carbon, in comparison to Sample 2, which is an as-synthesized strand. The typical experimental results [Fig. 1(c)] of the temperature dependence of the resistance of these SWNT strands present a semiconducting behavior (negative dR/dT) at low temperature (up to about 100 K), and a metalliclike behavior (positive dR/dT) at higher temperature ($T>100-150$ K). The measured resistance of the electron transport in SWNT bundles would be dominated by those tubes that are metallic in nature.[1] However, this is in contrast to the semiconducting behavior observed at low temperature. The existence of crossover phenomenon from a negative dR/dT to a positive dR/dT has been found before and considered as an intrinsic feature of electron transport in "metallic" SWNT ropes, although this behavior is not well understood.[14]

For the SWNT bundles that have small band gaps or psuedogaps,[8–11] we can simply express the conductivity of an entire SWNT strand as $\sigma = ne\mu_n + pe\mu_p$, where n and p are the carrier concentrations of n-type (electrons) and p-type (holes) carriers, respectively, and μ_n and μ_p are the electron and hole mobilities. The DOS near the energy gap of a one-dimensional (1D) metallic SWNT can be simplified as the one depicted in Fig. 1(d). The Fermi level E_F is set at zero energy, and the energy gap $E_g = E_c - E_v$ is the energy that separates the valence-band edge (E_v) and the conduction-band edge (E_c). We can then calculate the temperature dependence of the carrier concentrations of electrons and holes of the 1D metallic tube with a small energy gap.

As we reported in a previous publication,[15] and as discussed in terms of the tight-binding analysis,[1] the valence band and conduction band near the Fermi level in SWNTs are nearly symmetric. To simplify the analysis, we first assume that the Fermi level is in the middle of the energy gap, that is: $E_C - E_F = E_g/2$ and $E_F - E_V = E_g/2$. We will then express the temperature dependence of the resistance of the metallic nanotube with a small energy gap or pseudo-gap E_g as,

$$R = \frac{A_1}{\ln\left[1 + \exp\left(\frac{-E_g}{2K_BT}\right)\right]}. \qquad (1)$$

In Eq. (1), we utilize a simplified model in which we assume the contribution of the carrier mobility to be constant with respect to temperature. We present this calculated temperature dependence of the resistance of Samples 1 and 2 using Eq. (1), as the solid circles in Figs. 2(a) and 2(b), in comparison with experimental data [open squares in Fig. 2(a) and solid squares in Fig. 2(b)]. The constant A_1 was eliminated by normalizing the resistance $R(T)$ with R_0, where R_0 is the lowest resistance of the sample in the measured temperature region. The calculated energy gaps E_g from the curve fitting are 1.4 meV and 1.03 meV for Samples 1 and 2, respectively. One can clearly see that the simple model of Eq. (1) can describe the experimental results quite well in the low-temperature region for $T<200$ K, although less agreement is observed as the temperature is increased above 200 K. This simplified model indicates that the carrier concentration as a function of temperature is the dominant factor to the temperature dependence of the experimentally measured resistance of the long SWNT strands.

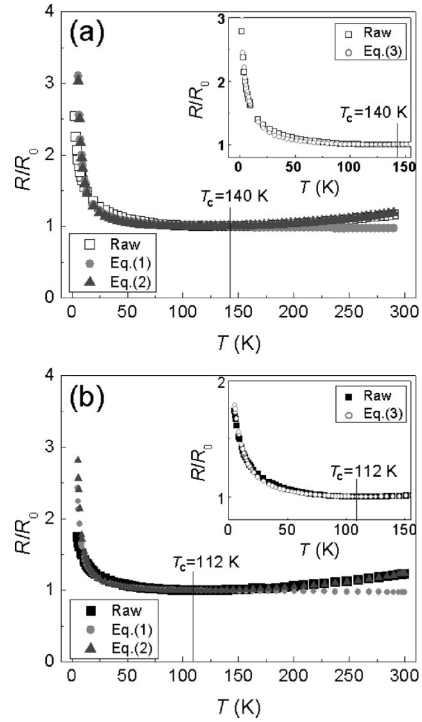

FIG. 2. (Color online) The relationship of the resistance of long SWNT strands as a function of temperature: (a) Sample 1, and (b) Sample 2. R_0 is the lowest resistance in the measured temperature region. The squares represent the experimental results. The solid circles and triangles are the calculated results from two models [using Eqs. (1) and (2), respectively]. [The results using Eq. (3) are presented in the insets (open circles).]

We further improved the simplified model of the above calculation by considering the temperature dependence of the carrier mobilities as well, which produces the following equation:

$$R = \frac{A_2}{\ln\left[1 + \exp\left(\frac{-E_g}{2K_BT}\right)\right]}(1 + CT^3). \tag{2}$$

The calculated temperature dependent resistances of the two SWNT samples using Eq. (2) are presented as the solid triangles in Figs. 2(a) and 2(b). The calculated result agrees very well with the experimental data. The calculated energy gaps E_g due to the model improvement adjust to be 1.6 meV and 1.21 meV for Samples 1 and 2, respectively. In this analysis, we assume that the DOS should be zero in the region of the band gap or pseudo-gap. The resistance will, therefore, approach infinity as the temperature goes to zero.

In the above calculations using Eqs. (1) and (2), we assume that the Fermi level E_F lies just in the middle of the small energy gap or pseudo-gap. The Fermi level in the real samples of the SWNT strands may be pinned at various locations inside the energy gap. The above assumption in the simplified model is attributed partly to the deviations of the calculated results from the experimental data in the low-temperature region ($T<10$ K). We could then utilize the Fermi level E_F as a fitting parameter to further improve the calculation and rewrite the expression of the resistance as

$$R = \frac{A_3}{\ln\left[1 + \exp\left(-\frac{d_1}{K_BT}\right)\right] + D\ln\left[1 + \exp\left(-\frac{d_2}{K_BT}\right)\right]}(1 + CT3), \tag{3}$$

where $d_1 = E_c - E_F$; $d_2 = E_F - E_v$; and $D = N_p\mu_p/N_n\mu_n$. The energy gap or pseudo-gap E_g is calculated from d_1 and d_2 by the relationship: $d_1 + d_2 = E_c - E_v = E_g$. The calculated results of the temperature dependence of the resistance, using Eq. (3), are shown in the insets of Figs. 2(a) and 2(b), where the open circles represent the calculated results and the squares represent the experimental data. It is worth mentioning that the agreement of the calculated results with experimental data is improved dramatically in the low-temperature region. We find an excellent agreement between the experimental and calculated data [from Eq. (3)] over the entire temperature range, when the calculated energy gap E_g is 1.85 meV and 1.7 meV for Samples 1 and 2, respectively. The Fermi level is very close to one of the band edges (E_c or E_v) with very small energies (about 0.1 meV to 0.15 meV), and is far away from the middle of the energy gap, similar to a pinned Fermi level in a doped semiconductor. The driving force behind the shift of the Fermi level needs further investigation.

The values of the super-small gaps of different samples lie in a very narrow range (1–3 meV), indicating that the super-small gaps are not influenced by catalyst impurities and amorphous carbon and might be an intrinsic property of the metallic SWNT bundles. We have used both ac and direct current power and got the same results, excluding the influence from a magnetic field. Due to the intrinsic continuity of the SWNT strands, we expect the super small gaps can provide evidence for a continuous conducting channel along individual SWNTs instead of electron hopping from tube to tube or from bundle to bundle.

From Ref. 14, we have extracted the temperature dependent resistance data of an individual SWNT rope [armchair (10, 10)] synthesized using a laser ablation technique and calculated the band gap of their SWNT ropes using our model. Even though less data are available at low temperatures, the calculated gap is also very small (about 2.7 meV, with the Fermi energy at 0.26 meV near one band edge), similar to our samples, implying that a super-small band gap in the range of 1–3 meV is an intrinsic property of the metallic SWNT bundles, regardless of synthesis methods and measurement methods.

We are not aware of any evidence in previous studies that the impurity energy levels from the band edges in carbon nanotubes are so small. The tight-binding analysis,[1] experimental measurements,[16] and *ab initio* density functional computations[15] indicated that the band gaps of semiconducting nanotubes with diameters larger than 0.75 nm are diameter dependent. Our *ab initio* calculations[15] revealed that the semiconducting SWNT (13, 0) has a band gap of 0.75 eV with a diameter of 1.02 nm, and the SWNT (17, 0) has a band gap of 0.54 eV with a diameter of 1.33 nm. The semiconducting nanotubes with diameters around 1.1 nm would have a band gap of ~0.5 to 0.6 eV, and these tubes would hardly contribute to the resistance measurements. Thus, we can exclude the band-gap contributions from semiconducting nanotubes. In addition, it is worth mentioning that our model only considers the electrical properties of the entire "*bulk*" nanotube materials instead of any specific individual (n,m) metallic nanotubes.

Furthermore, we should point out that the band gap is defined in our model for the calculation of electron transport properties in the region that the DOS should be zero. It is different from the V-shaped pseudo-gaps reported earlier.[8,9] In conclusion, the experimentally measured temperature dependence of the resistance of the SWNT strands strongly suggests the existence of a super-small energy gap or pseudo-gap of about 1–3 meV in metallic SWNT bundles.

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