Effects of Gas Adsorption and Collisions on Electrical Transport in Single-Walled Carbon Nanotubes

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Degassing of bundles of single-walled carbon nanotubes in vacuum at 500 K is found to drive the thermoelectric power (TEP) strongly negative, indicating that the degassed metallic tubes in a bundle are n type. The magnitude of the negative TEP indicates that important asymmetry in the electronic carbon π bands exists near the Fermi energy. Easily measurable increases in the TEP (−5–10 μV/K) and resistivity (2%–10%) are observed at 500 K upon exposure to N₂ and He, suggesting that even gas collisions with the nanotube wall can contribute significantly to the transport properties.

In this Letter, we report on the effects of gas adsorption and collisions on the thermopower and resistivity of mats of tangled single-walled nanotube (SWNT) bundles [1,2]. Our results demonstrate that previously published large positive thermopower data, including our own [3], should not be assigned to intrinsic SWNT behavior, but to transport in oxygen-doped SWNTs. The observations we present here likely impact the results of many previously published transport studies on SWNTs and SWNT materials exposed to ambient conditions. The thermoelectric power (S) of mats or thin pellets containing bundles of single-walled carbon nanotubes have been reported previously [3–5]. The previously published experimental data are in reasonable agreement, i.e., S has a dominant linear (diffusion) component (S ∝ |ε|/T; p-type metal) and is surprisingly large S(300 K) ∝ +45 μV/K. A second, smaller, contribution to S, in the form of a superimposed broad peak with a maximum in the range ∼80–90 K, is also present [5]. The broad peak has recently been tentatively assigned to Kondo effect involving a residual magnetic catalyst trapped within the bundles [5]. As pointed out previously [4], large values of the diffusion thermopower at 300 K are not consistent with the near-mirror symmetry of overlapping valence and conduction bands at EF reported for isolated metallic SWNT. Explanations for the breaking of the electron-hole symmetry in metallic tubes have been presented: tube-tube interactions within bundles [6], or significant changes in the electronic density of states due to impurities or 5–7 defects in the nanotube walls [7].

We find that the large positive thermopower of SWNT bundles exposed to air at 300 K decreases and then changes sign as physisorbed oxygen is removed from the sample in a high vacuum environment at elevated temperature (∼500 K), in agreement with unpublished results from the Berkeley group [8]. Here, we also report in situ measurements of S(T) and the four-probe resistance R(T) for vacuum-degassed or “empty” SWNT bundles in a mat, and also of degassed samples later exposed to 1 atm of N₂ or He. Even He gas is found to impose easily measurable effects on both S and R, consistent with changes in carrier lifetimes. We presume that this is due to gas collisions with the nanotube wall generating nonthermal phonons and dynamic defects. Very recently, elegant work has been reported by Kong et al. on individual semiconducting SWNTs used as resistive chemical sensors to detect small concentrations 2–200 ppm NO₂ and NH₃ [9]. NO₂ and NH₃ are known, respectively, to be an electron acceptor and an electron donor. They therefore proposed that the charge transfer between the tube wall and the adsorbed molecules was driving increases in the SWNT conductance of up to 3 orders of magnitude for exposure to as little as 200 ppm of NO₂ at ∼300 K [9].

The SWNT material studied here was obtained from CarboLex, Inc. and consisted of ∼50–70 vol% SWNT produced by the arc discharge method using a Ni-Y catalyst. The material was found to exhibit the characteristic T = 300 K Raman spectrum (514 nm excitation) published previously [10], including the radial breathing mode band at 186 cm⁻¹ and the stronger tangential mode band at 1593 cm⁻¹. The average diameter of these tubes is therefore close to that of a (10, 10) tube. Typical high-resolution scanning electron microscopy images showed that the tubes were present in bundles, with bundle diameters in the range 10–15 nm, i.e., containing ∼100–200 tubes. The SWNT material was removed from the growth chamber and handled in ambient conditions. It was not given any postsynthesis chemical or thermal treatment. Samples for study were prepared by lightly pressing the fibrous powder into ∼2 × 2 × 0.1 mm thin pellets or mats. S data were collected using a heat pulse technique described previously [11,12]. The four-probe resistance R was measured in a van der Pauw geometry using a lock-in amplifier by a standard low frequency ac method. All of the results discussed below were duplicated in several samples.

In Fig. 1 we plot the time evolution of thermopower S (Fig. 1a) and four-probe resistance R (Fig. 1b) at
the time dependence of the temperature during the admission of the same meaning as described for (a). Shown in the inset is normalized to sample resistance at $S$ to vacuum, 1 atm of $N_2$ initially saturated with air at ambient conditions. Fig. 1a and 1b. We concentrate first on the conditions for several days, then mounted in the apparatus which was evacuated to $\sim 10^{-6}$ Torr and heated from 300 to 500 K, reaching this temperature at point $A$ in Figs. 1a and 1b. We concentrate first on the $S$ data (Fig. 1a). As the sample was degassed in vacuum at 500 K ($A \rightarrow B$), $S$ decreased slowly over 15 h from an initial value $S(500$ K) = $+54 \mu$V/K, changed sign, and then eventually approached a constant value of $S(500$ K) = $-44 \mu$V/K near $B$. We identify the negative $S$ plateau in Fig. 1a near $B$ at $-44 \mu$V/K, with the signature of degassed or empty SWNT bundles. At point $B$ (Fig. 1a), we next isolated the sample chamber from the vacuum pump and, over $\sim 3$ min, introduced $\sim 1$ atm of ultrahigh purity (uhp) $N_2$ gas. $S(500$ K) then was observed to rise slowly from the “empty tube” value at $-44 \mu$V/K to a higher plateau at $-33 \mu$V/K. At $C$ we began a second $N_2$ cycle, first pumping between $C$ and $D$, then introducing 1 atm $N_2$ at $D$, as we did at $B$. During pumping, $S(500$ K) returned to the “empty bundle” value. Admitting $N_2$ again at $D$, $S(500$ K) returned to the previously obtained value of $-33 \mu$V/K. Pumping ($E \rightarrow F$) then reduced $S(500$ K) to the empty bundle value again. Next, we performed similar experiments with uhvp He for two successive cycles. $S(500$ K) cycled, in each case, between a negative plateau at $-28 \mu$V/K and the empty, or fully desorbed, value of $-44 \mu$V/K. Note that this “He-loaded” value ($-28 \mu$V/K) is more strongly upshifted than the $N_2$-loaded plateau ($-33 \mu$V/K). At points $A$ and $B$, and also later at points $E$ and $I$, after loading with $N_2$ and He, respectively, the sample was also cycled between $\sim 100$ and 500 K, and the $T$ dependence of $S$ and $R$ was recorded in situ. This $S(T)$ and $R(T)$ data will be discussed later.

In Fig. 1b, we plot the time evolution at $T = 500$ K of the normalized four-probe mat resistance, as the sample was cycled through the same series of experiments (vacuum, $N_2$-He exposure), as described above. The data are plotted as $R/R_A$, where $R_A$ is the four-probe resistance at point $A$ [13]. The labels $A \rightarrow J$ in Fig. 1b correspond to the same changes in sample environment as discussed above in reference to Fig. 1a. In all cases, whether the gas was $O_2$ (air), $N_2$, or He, the resistance decreased as the gas was removed from contact with the sample. As observed in Fig. 1a for $S(500$ K), $O_2$ removal took a significantly longer time to accomplish than observed for $N_2$ or He. This is indicative of a stronger binding of $O_2$ to the tube wall, consistent with weak charge transfer between SWNT and $O_2$. In every case (i.e., $O_2$, $N_2$, or He), degassing the sample at 500 K eventually depressed the resistance to the same minimum value (i.e., to the empty bundle value). Superimposed on the normalized resistivity data in Fig. 1b is the temperature change of the mat due to the introduction and removal of 1 atm of $N_2$ and He gas. This $1^\circ-2^\circ$ rise and fall in sample temperature is also applicable to the data in Fig. 1a and actually reduces the response of $S$ and $R/R_A$ to the gas. This point is deferred to later when the temperature dependence of $S$ and $R$ is discussed.

In Fig. 2, from top to bottom, we display the $T$ dependence of $\Delta R/R$ or $\rho_N(T)$ for He-loaded ($I$), $N_2$-loaded ($E$), empty ($B$), and $O_2$-loaded ($A$) mats (all data are from the same sample), where the letter in parentheses indicates the point in the sample evolution in Fig. 1 when the sample was cycled to low $T$ and back to 500 K in the respective gas (1 atm) environment. For clarity, these normalized resistivity curves have been displaced vertically by the amount indicated in parentheses to the left of each curve. Only the mat with degassed or empty bundles exhibits $d\rho_N/dT > 0$, and only above 400 K is this metallic contribution evident. The small rise $\sim 1–2$ K in the sample temperature (see inset of Fig. 1b) due to the introduction of $N_2$ and He gas therefore would be expected to induce a negative $d\rho/dT$, consistent with the $\rho_N$ data in
Fig. 2. Normalized resistivity for mats of SWNT bundles vs temperature. The letters A, B, E, and I have the same meaning as in Figs. 1a and 1b (see caption to Fig. 1a). N2 and He were admitted to a pressure of ~1 atm at 500 K, sealed the system, and cooled down. The curves have been offset vertically by the amount indicated in parentheses to the left of each curve.

In Fig. 3, we plot the T dependence of the thermopower of the same SWNT mat sample collected at several points in the time evolution of the sample (Figs. 1a and 1b): point A (air-saturated mat; data collected in vacuum), B (degassed or empty mat; data collected in vacuum), E (N2-loaded mat; data collected in 1 atm N2), and point I (He-loaded mat; data collected in 1 atm He). Data collected on cooling and warming overlapped well in every case. As can be seen in the figure, independent of whether the bundles were saturated with O2 (air), N2, or He, or were empty (degassed), the thermopower is always dominated by a linear contribution from free carrier diffusion, i.e., \( S \sim T \), indicating that \( S \) is associated primarily with metallic tubes in a mat (semiconducting tubes would be expected to exhibit the behavior \( S \sim 1/T \)). We conclude that the magnitude, the slope (\( \mu \text{V/K}^2 \)), and even the sign of the \( S \) data in Fig. 3 depend on the nature of the surface interaction of the gas and the \( \pi \) electrons in the SWNTs. The \( S \) data were fit to \( S = a + bT \) and the parameter values for (a and b) appear in the inset of Fig. 3. The dotted curve in Fig. 3, which overlaps the solid circles of curve A (air saturated), represents data taken to lower \( T \) on a different sample, and is shown for comparison, and also to indicate how \( S \) should approach zero as \( T \rightarrow 0 \). Early theoretical calculations of the thermopower for armchair symmetry tubes [4] found that \( S \sim 0 \mu \text{V/K} \). This was attributed to the calculated mirror symmetry of the coexisting electrons and holes in overlapping \( \pi \) bands. In this case, the cancellation of electron and hole thermopowers can be appreciated using the standard expression for \( S \) arising from carriers in two bands [15], which is given by \( S = (\sigma_1 S_1 + \sigma_2 S_2)/(\sigma_1 + \sigma_2) \), where \( \sigma_j \) is the electrical conductivity, \( S_j \) is the thermopower of the \( j = 1, 2 \) bands, and where the electron \( (S_1) \) and hole \( (S_2) \) diffusion thermopower depends inversely on the Fermi energy, \( S_j \sim T/E_{F,j} \). With mirror symmetry in the conduction and valence bands, \( E_{F,1} = -E_{F,2} \) and \( \sigma_1 = \sigma_2 \) (equal band masses and carrier lifetimes), and therefore it is evident from this thermopower relation that we should expect \( S \sim 0 \mu \text{V/K} \).

We discuss the temperature dependence of thermopower of empty SWNT bundles first. The fact that the linear component of \( S \) for the degassed samples is large and negative [i.e., \( S(300 \text{K}) = -30 \mu \text{V/K} \)] suggests that the mirror band symmetry for isolated metallic SWNTs may not actually exist. The symmetry, however, may be sufficiently disturbed or broken by tube-tube interactions [6] or defect states [7]. Perhaps more sophisticated energy band calculations for isolated tubes may reveal significant asymmetry between the conduction and the valence states to explain the large negative thermopower observed.
here. It is apparent that the electron contribution dominates the thermopower of the degassed or empty mats, i.e., $|\sigma_1 S_1| > |\sigma_2 S_2|$. Thus, an imbalance in either $S_1$ and $\sigma_1$ or both, relative to that of the hole band, drives the total thermopower negative.

In the case of $O_2$-loaded SWNT bundles (air saturated), relative to that of degassed or empty bundles, the thermopower changes sign and becomes strongly positive [i.e., $S(300 \text{ K}) \sim 48 \mu \text{V/K}$]. This large $O_2$-induced swing in the thermopower suggests to us that weak charge (electron) transfer from the tube wall to the adsorbed $O_2$ has likely taken place, creating a negatively charged defect. $E_F$ is therefore depressed well below its intrinsic value, and would probably be pinned at $O_2$-derived defect states overlapping the hole band. As the electronic density of states in the quasi-one-dimensional electronic bands is quite low compared to ordinary 3D bands, it is reasonable to expect significant movement in the Fermi energy without requiring too much charge transfer per adsorbed $O_2$. $O_2$ has also been found to have a dramatic effect on the resistivity of solid $C_{60}$ [16,17]. In the case of $C_{60}$, the changes we observe for added $N_2$ and $He$ near $500 \text{ K}$ is therefore ascribed to changes in the electronic density of states of $C_{60}$ cages, even though all of the $C$-$C$ bonds are satisfied. A small charge transfer between $C_{60}$ and $O_2$ has also been proposed to explain the large dipole moments probed in dielectric function measurements in the range $0.5 \text{ mHz} \rightarrow 100 \text{ kHz}$ [17]. Kong et al. [9], in their recent report on SWNT chemical sensors, refer to extrinsic $n$-type behavior in their isolated, semiconducting SWNT. In light of the present work, it is reasonable to propose that this $n$-type behavior in their semiconducting tubes is also due to absorbed $O_2$ on the tube wall.

We finally discuss the effect of $N_2$ and $He$ loading on $S(500 \text{ K})$ and $\rho_\phi / \rho_A (500 \text{ K})$ shown, respectively, in Figs. 1a and 1b. In the case of these gases, we expect that the charge transfer between the adsorbed gas and the tube wall is negligible. It should be noted that the effects are not small, leading to changes on the order of $2\%$-$10\%$ in $R(500 \text{ K})$. Without charge transfer, the changes we observe in $R(500 \text{ K})$ are tentatively assigned to changes in the electron and hole free carrier lifetimes (or, equivalently, the carrier mobility). These large changes in the carrier lifetime are assigned either to increased carrier scattering from dynamic defect states associated with momentarily adsorbed gas or to nonthermal, localized SWNT phonons generated by collisions of the gas molecules with the tube walls. It is clear that the transport properties of SWNT bundles are quite sensitive to even inert gases present in the sample chamber, at least for $T > 100 \text{ K}$.

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**Note added.** After this article was submitted, A. Zettl and co-workers published an article [18] also dealing with the dramatic effects of $O_2$ adsorbed on SWNTs.

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[13] $R/R_A = \rho / \rho_A$, where $\rho$ and $\rho_A$ are resistivities. That is, the geometrical factor cancels out of the resistance ratio.

[14] The same argument can be made for the $S$ response plotted in Fig. 1a. Since $d[S]/dT > 0$ (Fig. 3), the small rise in sample $T$ during gas input actually would be expected to reduce the thermopower response. The $\Delta[S] < 0$ we observe for added $N_2$ and $He$ near $500 \text{ K}$ is therefore assigned to the effects of gas collisions with the tube wall and not to this small temperature increase.


