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

G. U. Sumanasekera,[1] C. K. W. Adu,[1] S. Fang,[2] and P. C. Eklund[1,*]
[1] *Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802*
[2] *CarboLex Incorporated, Lexington, Kentucky 40505*

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Degassing of bundles of single-walled carbon nanotubes in vacuum at 500 K is found to drive the thermoelectricpower (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 ($\sim 5-10\ \mu$V/K) and resistivity (2%−10%) are observed at 500 K upon exposure to N_2 and He, suggesting that even gas collisions with the nanotube wall can contribute significantly to the transport properties.

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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 ($S \sim |c|T$; p-type metal) and is surprisingly large $S(300\text{ K}) \sim +45\ \mu$V/K. A second, smaller, contribution to S, in the form of a superimposed broad peak with a maximum in the range $\sim$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 E_F 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 ($\sim$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 N_2 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 NO_2 and NH_3 [9]. NO_2 and NH_3 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 NO_2 at $\sim$300 K [9].

The SWNT material studied here was obtained from CarboLex, Inc. and consisted of $\sim$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 $\sim$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 $\sim 2 \times 2 \times 0.1$ 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

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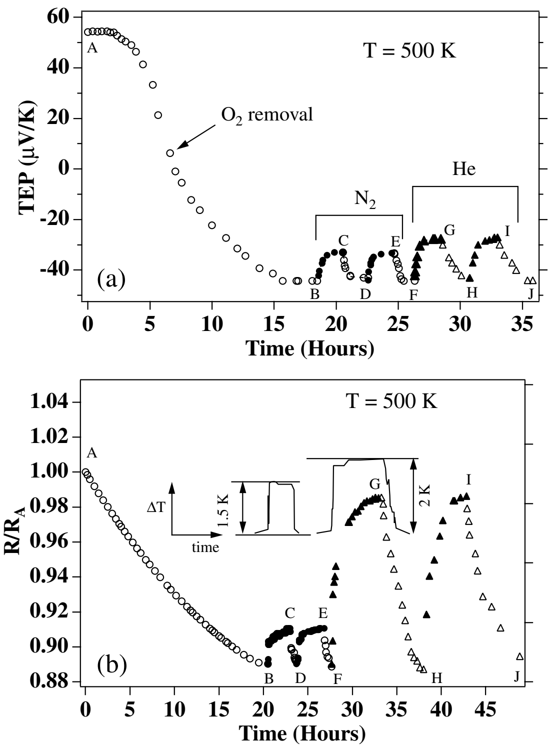


FIG. 1. (a) Thermopower S vs time for a mat of SWNTs at $T = 500$ K initially saturated with air at ambient conditions. The sample is under dynamic vacuum when open symbols are used, and dark symbols represent intervals when N_2 and He are present. N_2 is introduced at B and D; He is introduced at F and H. Vacuum pumping is applied at A, C, E, G, and I. (b) Four-probe resistance ratio of SWNT mat at 500 K vs time. Data normalized to sample resistance at A. Points A through I have the same meaning as described for (a). Shown in the inset is the time dependence of the temperature during the admission of each gas and subsequent pumping.

$T = 500$ K for a typical sample successively exposed to vacuum, 1 atm of N_2 and He gases. Open symbols represent the sample in dynamic vacuum and dark symbols represent intervals when gases are present. The sample was previously air saturated under ambient 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 $S(500\text{ K}) = +54\ \mu\text{V/K}$, changed sign, and then eventually approached a constant value of $S(500\text{ K}) = -44\ \mu\text{V/K}$ near B. We identify the negative S plateau in Fig. 1a near B at $-44\ \mu\text{V/K}$, 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 ~3 min, introduced ~1 atm of ultrahigh purity (uhp) N_2 gas. $S(500\text{ K})$ then was observed to rise slowly from the "empty tube" value at $-44\ \mu\text{V/K}$ to a higher plateau at $-33\ \mu\text{V/K}$. 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, $S(500\text{ K})$ returned to the "empty bundle" value. Admitting N_2 again at D, $S(500\text{ K})$ returned to the previously obtained value of -33 V/K. Pumping ($E \rightarrow F$) then reduced $S(500\text{ K})$ to the empty bundle value again. Next, we performed similar experiments with uhp He for two successive cycles. $S(500\text{ K})$ cycled, in each case, between a negative plateau at $-28\ \mu\text{V/K}$ and the empty, or fully desorbed, value of $-44\ \mu\text{V/K}$. Note that this "He-loaded" value ($-28\ \mu\text{V/K}$) is more strongly upshifted than the N_2-loaded plateau ($-33\ \mu\text{V/K}$). 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 ~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 $S(500\text{ K})$, 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°–2° 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 ~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 ρ_N data in

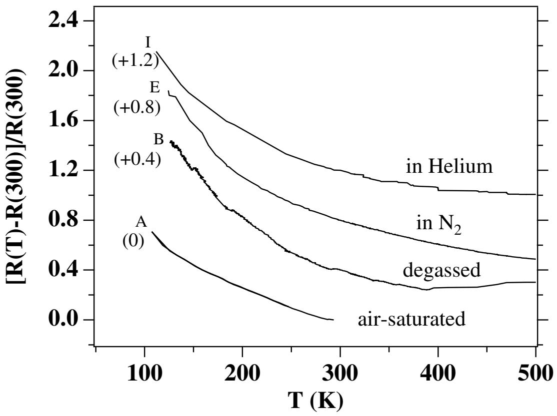
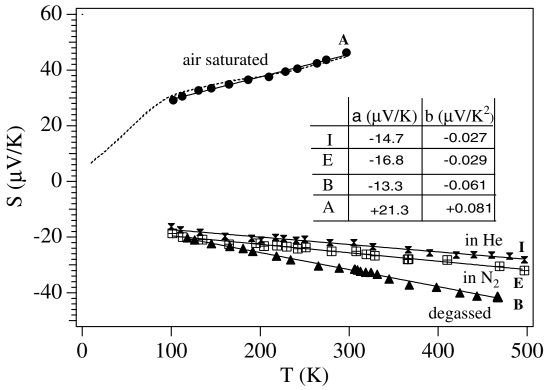


FIG. 2. Normalized resistivity for mats of SWNT bundles vs temperature. The letters A, B, E, and I have the same meaning as in Figs. 1a and 1b (see caption to Fig. 1a). N$_2$ and He were admitted to a pressure of ~1 atm at 500 K, sealed the system, and cooled down. The curves have been offset vertically by the amount indicated in parentheses to the left of each curve.



	a (μV/K)	b (μV/K^2)
I	-14.7	-0.027
E	-16.8	-0.029
B	-13.3	-0.061
A	+21.3	+0.081

FIG. 3. Thermoelectric power of SWNT mat vs temperature for air-saturated mat (A), He loaded (I), N$_2$ loaded (E), and degassed or empty (B). The dotted line represents data from a second air-saturated sample taken to lower T. The straight lines through the curves are fits to the expression $S = a + bT$. Values for a and b appear in the inset of the figure.

Fig. 2. Thus, as mentioned above, this small T-increase actually reduces the response R/R_A to the introduction of the gas. The positive step in R/R_A is therefore identified with gas collisions with the walls of the SWNTs, and not the result of a small step in sample T as the gas is introduced [14]. Fortunately, the thermopower is not sensitive to the contact resistance [4], and the effects of gas loading on the electronic properties of the mats can be probed more directly with the thermopower than the resistivity (cf. Fig. 1a). Perhaps an unexpected result is the easily measurable effects on S and R at 1 atm of He and N$_2$ in the chamber. This, we believe, is the direct result of the quasi-one-dimensional nature of the conduction within a bundle and the fact that most of the C atoms are accessible to the gas, i.e., they are surface atoms. The sensitivity of individual semiconducting SWNTs to ppm levels of NO$_2$ and NH$_3$ has been demonstrated recently [9]. But, for these gases, charge transfer to the tube walls is expected, which is certainly not the case for N$_2$ and He, where the changes in the transport properties must be due primarily to changes in the free carrier scattering attributed to gas contact.

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 (N$_2$-loaded mat; data collected in 1 atm N$_2$), 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 O$_2$ (air), N$_2$, 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 (μV/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 π 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 $S \sim 0$ μV/K. This was attributed to the calculated mirror symmetry of the coexisting electrons and holes in overlapping π 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 σ_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 $S \sim 0$ μV/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., $S(300\ \text{K}) = -30$ μV/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 σ_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}, momentary exposure to laboratory air induces as much as 4 orders of magnitude decrease in the resistivity [17], demonstrating that O_2 can "react" with the 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 mHz → 100 kHz [17]. Kong *et al.* [9], in their recent report on SWNT chemical sensors, refer to extrinsic p-type behavior in their isolated, semiconducting SWNT. In light of the present work, it is reasonable to propose that this p-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 $\rho_N(500\text{ K})$ 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 due 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 $T > 100$ 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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*To whom correspondence should be addressed.
Email address: pce3@psu.edu

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[13] $R/R_A = \rho/\rho_A$, where ρ and ρ_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 K is therefore assigned to the effects of gas collisions with the tube wall and not to this small temperature increase.

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