RAPID COMMUNICATIONS

Transport properties of alkali-metal-doped single-wall carbon nanotubes

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We report *in situ* measurements of four-probe dc resistance (R) and thermopower (S) of Cs- and K-doped single-wall carbon nanotube (SWNT) mats as a function of a doping and temperature (T). With increasing dopant exposure, the mat resistance has been found to first decrease and then increase, exhibiting a minimum for optimal Cs doping. In contrast, for K doping, the mat resistance decreased monotonically and saturated. This unexpected result suggests that the diameter of the alkali-metal ion plays a role in the transport properties of the tube bundles. A doping-induced decrease in R by factors of ~120 and ~40 were observed for Cs- and K-doped SWNT mats, respectively. The low-temperature upturn of $R(T)$ observed in all pristine SWNT samples was progressively suppressed with increased K doping. The optimally Cs-doped sample exhibited a positive dR/dT over the entire range of measurement (80 K$<T<$300 K). In contrast to the anomalously large positive $S_{300 K}\sim+40-+50$ μV/K observed in pristine SWNT at room temperature, the Cs-doped samples exhibited a small negative $S\sim-7$ μV/K as expected for an ordinary metal. [S0163-1829(98)52032-2]

Single-wall carbon nanotube (SWNT) mats have been found by several groups to exhibit metallic-type behavior (i.e., positive dR/dT) at high temperatures $T>T^*$, and non-metallic behavior ($dR/dT<0$) at $T<T^*$.[1–4] The values for T^*, the crossover temperature between the metallic and non-metallic regimes, vary from ~35 K in a single defect-free bundle to ~150–300 K and higher in mats.[3] Several models have been proposed to account for this unusual behavior, including weak localization,[2,4] heterogeneous conduction,[3] and scattering by magnetic catalyst impurities,[5] but no consensus has been established so far. Also, it is not yet clear from a theoretical perspective to what extent the tube-tube interactions within a bundle[6] will affect electrical transport and other physical properties.

Doping of SWNT bundles with either donors or acceptors is expected to shift the Fermi energy E_F in the electronic band structure and can provide valuable insight into the electronic conduction mechanism. An implicit, but powerful motivation to study alkali-metal-doped SWNT's is to search for possible new superconducting phases, in analogy with superconducting alkali-metal-doped graphite and solid C_{60}. So far, only a very few measurements of transport properties of doped SWNT's have been reported.[1,7] In particular, it has been found that upon either potassium,[1] bromine,[1] or iodine[7] doping, the dc resistivity (R) of SWNT mats decreased by a factor of ~30–50, and the metallic behavior (i.e., $dR/dT>0$) was extended to lower temperatures.[1] In this work, we investigate the *in situ* dc resistance and thermopower of both laser- and arc-derived SWNT mats as a function of Cs and K doping. Our data show the unexpected result that the *identity* of the alkali-metal dopant plays an important role in the electronic properties of the doped samples.

Mats of tangled SWNT bundles used in this work have been synthesized by either the pulsed laser vaporization
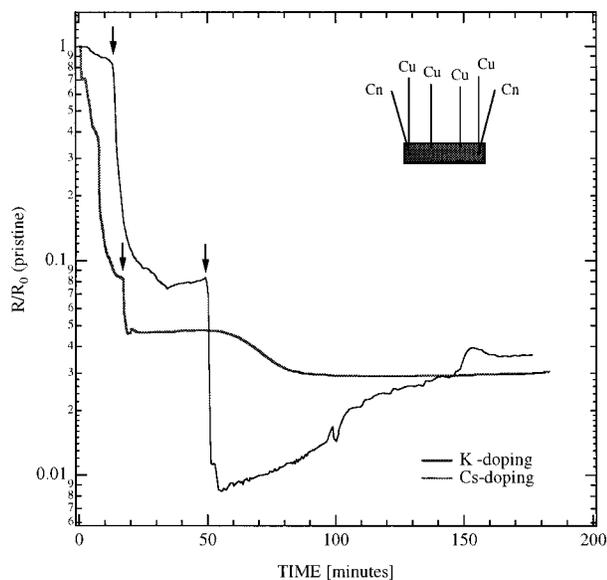
FIG. 1. A typical *in situ* variation of four-probe dc resistance R of alkali-metal-doped SWNT mats (normalized to the $T=300$ K resistance of the pristine SWNT mat) as a function of exposure time to Cs and K vapor. The inset shows the arrangement of copper (Cu)-constantan (Cn) thermocouples and two additional copper leads used to measure thermopower and four-probe resistance at the same time.

(PLV) (Ref. 8) or arc plasma[9] techniques. The PLV material was obtained from Rice University, and the arc-derived mats were synthesized at the University of Kentucky. The as-synthesized SWNT mats were characterized by x-ray diffraction and Raman-scattering spectroscopy and found to be quite similar, containing a narrow distribution of SWNT bundles with a mean tube diameter approximately equal to that of a (10,10) armchair tube.[10]

The doping-induced change of the thermopower, or Seebeck coefficient (S), and R were studied in a vertical glass reactor with ~20-mm inner diameter $x\sim20$ cm in length equipped with a $2\frac{3}{4}$-in. knife-edge flange sealed via a Cu-gasket to a standard multipin feedthrough flange. For *in situ* transport measurements, two Cu-constantan thermocouples and two Cu wires were attached to the SWNT mat or pellet using pressure contacts (Fig. 1, inset). In our dynamic thermopower measurements, a heat pulse was applied to one end of the sample to generate a maximum temperature difference $\Delta T\sim0.5$ K. The Seebeck coefficient $S=\Delta V/\Delta T$ was obtained using the analog subtraction method.[11] The sample holder with the SWNT sample attached to the electrical leads was loaded into the glass reactor together with a small, break-seal ampoule containing the alkali metal. The reactor was evacuated through a glass sidearm to $\sim10^{-6}$ Torr, back-filled with ~100 Torr of He gas (to improve thermal exchange) and sealed. The alkali metal was then released by shaking the reactor and breaking the break-seal on the alkali-metal-containing ampoule. The surface of the alkali metal remained shiny throughout the experiment indicating the absence of any significant amount of oxygen or water in the reactor.

The reactor was positioned in a temperature gradient in a vertical furnace and heated to vaporize the alkali metal. The temperature gradient was chosen to provide efficient trans-
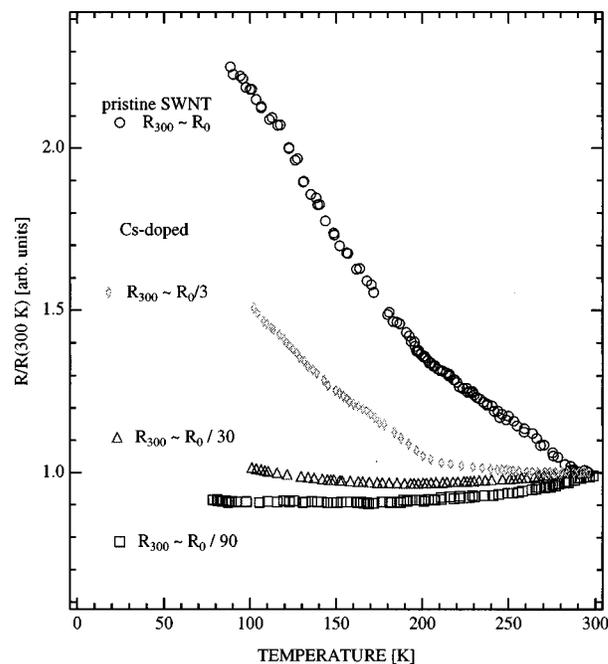

FIG. 2. Temperature dependence of four-probe resistance R of pristine and Cs-doped SWNT mats (normalized to their respective room-temperature values) for several doping levels.

port of alkali metal from the bottom of the reactor up to the sample holder, avoiding condensation of the unreacted alkali metal layer on the surface of the sample. At any time during the doping, we were able to stop the reaction by cooling the furnace and then measure the temperature dependence of R (Fig. 2) or S (Fig. 3) between 300 and 77 K at a fixed dopant concentration by lowering the reactor into a dewar of liquid
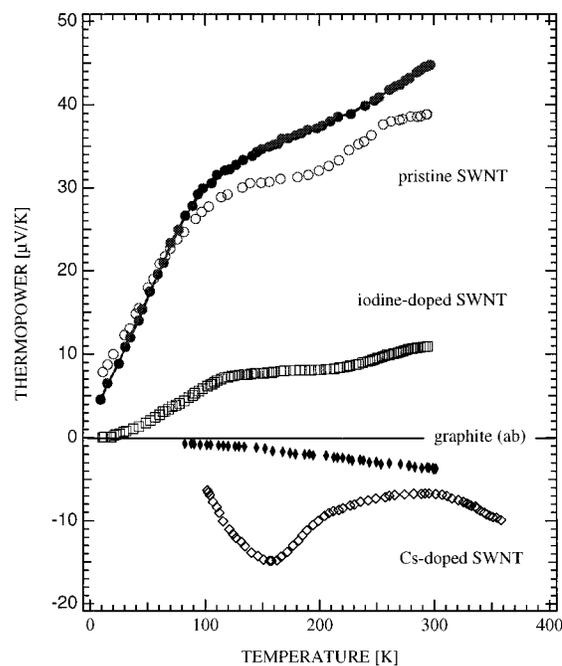

FIG. 3. Temperature dependence of thermopower of two pristine, saturation iodine-doped and lightly ($R/R_0\sim1/3$) Cs-doped SWNT mats. Data for in-plane thermopower for chemical-vapor-deposition grown graphite film are also shown for comparison.

nitrogen. Further doping could then be carried out by repositioning the reactor in the furnace. The results reported here were reproduced in several independent runs with both laser- and arc-produced SWNT samples.

Figure 1 shows a typical *in situ* variation of the resistance R (normalized to the resistance of pristine SWNT mat R_0) with exposure time to Cs and K vapor. An initial drop in R was observed when the alkali-metal temperature reached $\sim 200\,°C$ (Cs) or $\sim 250\,°C$ (K). Further sharp drops in R (indicated with arrows in Fig. 1) were observed to coincide with the times when the furnace temperature was stepped up by another $\sim 10\,°C$. We have increased the furnace temperature in steps in order to be able to observe the diffusion kinetics. The kinetics was found to be very fast, on the order of 1–5 min, in agreement with previous observations.[1] The resistance change $(R/R_0)_{300\,K}$ (where R and R_0 refer to doped and pristine mats, respectively) was observed to be alkali-metal dependent: the maximum reduction was found to be $\sim 1/100$–$1/120$ for Cs and $\sim 1/30$–$1/40$ for K. As shown in Fig. 2, for continued exposure of SWNT mat to Cs vapor, after an initial rapid decrease, R passed through a well-defined minimum, and then *increased* with further doping, saturating at $R/R_0 \sim 1/30$. In sharp contrast to this behavior, the exposure of SWNT mat to K produces a monotonically decreasing R that saturates at $R/R_0 \sim 1/30$–$1/40$, close to the value obtained in saturation-doped Cs-SWNT samples. Thus, unless the alkali-metal doping is carried out slowly *in situ*, one can easily miss this significant difference between Cs and K dopants. The origin of this different behavior may be related to the larger size of the Cs^+ ion (3.34 Å) as compared to the diameter of the K^+ ion (2.66 Å). The recent studies of iodine,[7] K, Cs,[12] and nitric acid[13] intercalation into SWNT bundles have indicated that intercalants reside in the interstitial channels between the tubes. Intercalation of large ions, such as Cs, would push the tubes apart, thereby decreasing the π-electronic overlap between the neighboring tubes. In contrast, the relatively smaller K^+ ions can fit into interstitial channels inside the SWNT bundle (diameter ~ 2.6 Å) almost without lattice expansion, and therefore would have much less effect on tube-tube separation. Our doping data and these structural considerations imply that interaction between the tubes may be an important factor for the electronic properties of SWNT ropes, as discussed in Ref. 6.

The results for $R(T)/R_{300\,K}$ vs T for Cs-doped SWNT mats are plotted in Fig. 2 for several doping levels, where $R_{300\,K}$ is the resistance of the doped mat at 300 K. As can be seen in the figure, the most apparent effect of Cs doping is to progressively suppress the temperature T^* and magnitude of the R upturn at low temperatures ($T < T^*$). It is important to note that the upturn is completely eliminated in the optimally doped Cs-SWNT sample (i.e., Cs-doping level that minimizes $R_{300\,K}$). In the optimally doped sample, we find that the resistance was essentially temperature independent below $T \sim 200$ K, and increased nearly linearly with T at higher temperatures. In contrast, the saturation-doped Cs-SWNT samples still exhibited an upturn ($dR/dT < 0$) for $T < 200$ K. In the K-doped samples, the R upturn at $T < T^*$ was also observed to be pushed to lower temperatures with the increasing K uptake. However, the negative dR/dT region persisted even in the saturation K-doped SWNT sample, re-
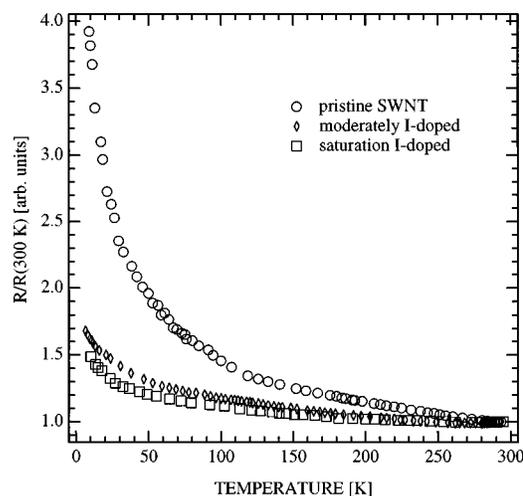

FIG. 4. Temperature dependence of four-probe resistance R of pristine and iodine-doped SWNT mats (normalized to their respective room-temperature values) for two doping levels.

sembling the behavior of the moderately Cs-doped SWNT [$R/R_0 \sim 1/30$ curve (triangles) in Fig. 2].

It is interesting to compare transport properties of the K- and Cs-doped (donor) SWNT's to the results obtained with the iodine-doped (acceptor) SWNT's.[7] The saturation I-doped SWNT mats exhibit $(R/R_0)_{300\,K} \sim 1/40$, similar to the saturation alkali-metal-doped SWNT samples.[7] However, in contrast to the alkali-metal doping, the iodine-doped mats did not exhibit positive dR/dT behavior for any T in the range of our study ($10 < T < 300$ K), even in the case of saturation doping (Fig. 4). The main effect of iodine doping was to reduce the temperature dependence of R. For example, the ratio $R_{10}/R_{300} \sim 4$ found in pristine SWNT mats was reduced to $R_{10}/R_{300} \sim 1.5$ in the saturation I-doped SWNT mats (Fig. 4). This response to acceptor doping is distinctly different from that of alkali-metal doping, where a positive dR/dT behavior appears at high T for low doping and shifts to progressively lower temperatures as the doping level increases. Comparison of the iodine- and K, Cs-doped SWNT data implies the presence of an *asymmetry* in transport properties of donor- and acceptor-doped SWNT's. A possible explanation for this asymmetry may be that, contrary to the theoretical predictions,[14] the electronic band structure for an individual nanotube is not symmetric.

Of course, it is important to note that the density of free charge carriers may be different in the iodine- and alkali metal-doped SWNT's, mainly because iodine has been shown to be intercalated as $(I_3)^-$ and $(I_5)^-$ polyiodide chains (one charge per three or five iodine atoms),[7] while alkali-metals intercalate as K^+ or Cs^+ species (one charge per atom). As a result, even though the dopant-to-carbon ratio in the saturation-doped samples is 1:12 for iodine,[7] not very different from 1:8 for K and Cs,[12] iodine doping is expected to create only 1 conduction hole per ~ 40–60 carbon atoms vs 1 conduction electron per ~ 8 carbon atoms in the cases of alkali-metal doping. Therefore, the density of free charge carriers in the saturation I-doped SWNT's will be 7 to 8 times lower as compared to the saturation K- and Cs-doped samples. However, the observed asymmetry is not only quantitative, but qualitative, that is, the temperature-

dependent behaviors of the resistance in iodine-doped and alkali-metal-doped SWNT's are clearly different. For that reason, it seems unlikely that the asymmetry in electronic properties is entirely due to the difference in density of charge carriers, but rather might reflect the underlying asymmetry in electronic band structure. The reason for this asymmetry is, as yet, unknown.

We next address the effect of Cs-doping on the thermopower of SWNT mats. Our pristine SWNT samples exhibit a large, positive $S_{300 K} \sim 40-50 \mu V/K$ that decreases with cooling (Fig. 3), in a good agreement with the earlier results.[4] The magnitude of $S_{300 K}$ for SWNT's is surprising, as the in-plane thermopower of semimetallic graphite is much smaller and negative, i.e., $S_{300 K} \sim -4 \mu V/K$ (Fig. 3). Metallic SWNT's which might be expected to dominate the conductivity-weighted transport properties, are expected to exhibit $S \sim 0 \mu V/K$ similar to graphite,[4] and therefore the origin of this unusually large S for SWNT's is not clear at present. In iodine-doped SWNT's, S remains positive, but its magnitude at $T = 300$ K is decreased by a factor of 3–4 from that in pristine mats, indicating that iodine doping creates a large number of free hole carriers. Upon Cs doping, S changes sign to negative and its magnitude drops significantly (Fig. 3). At high temperatures ($T > 300$ K), $S(T)$ for the lightly Cs-doped SWNT sample ($R/R_0 \sim 1/3$) increases linearly with T, consistent with the diffusion thermopower term in ordinary metals and in graphite (Fig. 3). However, $S(T)$ for the Cs-doped SWNT sample exhibits a pronounced peak of unknown origin around $T \sim 160$ K. This peak might be related to phonon drag or some other mechanism to be elucidated. Further, thermopower studies of Cs-doped SWNT mats and, in particular, on optimally doped mats, are

in progress and will be reported elsewhere.

Finally, it is interesting to note that the observed magnitude of the doping-induced resistivity decreases in SWNT's ($R/R_0 \sim 1/40-1/120$) is notably higher (by a factor of 2–6) than that reported earlier in graphite intercalation compounds (GIC's) ($R/R_0 \sim 1/4-1/20$).[15] Since the in-plane resistivity value for graphite is $R_{300 K} \sim 40 \mu\Omega$ cm, a ~ 20-fold decrease in R, as observed in SbF$_5$-GIC,[15] reduces $R_{300 K}$ to a value near that of copper ($R_{Cu} \sim 1.5 \mu\Omega$ cm). Unfortunately, the volume resistivity of SWNT bundles is difficult to evaluate due to complications with the geometrical factor related, in particular, to an unknown space-filling factor for the bundles within a mat. Resistivity estimates range from $\sim 0.01 \Omega$ cm (Ref. 1) to 600 $\mu\Omega$ cm for pristine SWNT mats, and a value of 100 $\mu\Omega$ cm has been reported for a single SWNT rope.[2,3] These resistivity values are 2.5 to 250 times more than those of graphite. It remains to be seen how the volume resistivities of doped SWNT mats and single ropes relate to those of copper. If the value reported for a pristine single rope[3] is correct, then the doped SWNT ropes would exhibit remarkably low values of $R_{300 K} \sim 2.5$ to ~ 0.8 $\mu\Omega$ cm, which are comparable to or even lower than those of R_{Cu}.

Note added in proof: For further discussion on the different effects of donor- and acceptor-doping on electrical transport in 5 WNTs, see Ref. 16.

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[1] R. S. Lee *et al.*, Nature (London) **388**, 255 (1997).

[2] J. E. Fischer *et al.*, Phys. Rev. B **55**, R4921 (1997).

[3] A. B. Kaiser, G. Dusberg, and S. Roth, Phys. Rev. B **57**, 1418 (1998).

[4] J. Hone *et al.*, Phys. Rev. Lett. **80**, 1042 (1998).

[5] G. T. Kim *et al.*, Bull. Am. Phys. Soc. **43**, 535 (1998).

[6] P. Delaney, H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, Nature (London) **391**, 466 (1998).

[7] L. Grigorian *et al.*, Phys. Rev. Lett. **80**, 5560 (1998).

[8] A. Thess *et al.*, Science **273**, 483 (1996).

[9] C. Journet *et al.*, Nature (London) **388**, 756 (1997).

[10] A. M. Rao *et al.*, Science **275**, 187 (1997).

[11] P. C. Eklund and A. K. Mabatah, Rev. Sci. Instrum. **48**, 775 (1977).

[12] S. Suzuki, C. Bower, K. Tanigaki, and O. Zhou, Chem. Phys. Lett **285**, 481 (1998).

[13] C. Bower, A. Kleinhammes, Y. Wu, and O. Zhou, Chem. Phys. Lett. **285**, 481 (1998).

[14] N. Hamada, S.-I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[15] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[16] L. Grigorian *et al.* (unpublished).