PHYSICAL REVIEW B VOLUME 61, NUMBER 7 15 FEBRUARY 2000-I

Transport properties of a potassium-doped single-wall carbon nanotube rope

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(Received 11 August 1999; revised manuscript received 20 October 1999)

Four-probe resistance vs temperature and gate voltage are reported for an individual single-wall carbon nanotube rope before and after doping *in situ* with potassium. All the features in $R(T)$ from unoriented bulk material, before and after doping, are qualitatively reproduced by the rope data. The 5.3 K conductance of the pristine rope decreases with positive gate voltage, while G vs V_g becomes featureless after K doping.

Single-walled carbon nanotubes (SWNT's) are electronically one dimensional and can be intrinsically metallic or semiconducting depending on chirality.[1] They coalesce during synthesis into crystalline ''ropes'' consisting of tens to hundreds of tubes packed in a triangular lattice, with a random distribution of chiralities[2–4] but a fairly narrow diameter range around 1.4 nm.[5,6] As-grown material consists of a low-density tangled network of ropes, referred to as ''mat.''

The resistance of SWNT can be modulated by adding or removing carriers from the system. Mats can be chemically doped with donors or acceptors,[7–9] both of which cause dramatic decreases in resistance. However, this does not establish whether doping enhances the conductance of the ropes or merely improves rope-rope contacts. Individual tubes can also be electrostatically ''doped'' using a field-effect transistor (FET) configuration.[10,11] In semiconducting tubes the conductance G decreases dramatically with positive gate voltage V_g while metallic ones show no V_g dependence.

Here we use both schemes to tune E_F in a large nanotube rope.[5] Ropes have the advantage of mimicking the smallest conducting unit in a mat without complications from the tangled morphology. They should also be less sensitive than single tubes to perturbations from metal contacts. The disadvantage is that a given rope contains an unknown ratio of metallic and semiconducting tubes. Four-probe R vs T and G vs V_g were measured on a single rope before and after *in situ* doping with potassium. Our goals were to determine if the unusual features in $R(T)$ of pristine and doped mats[8,12] are intrinsic or rather due to the complex morphology, and to establish that doping-induced charge transfer is responsible for conductivity enhancement in a system with no rope-rope contacts.

Figure 1 shows an atomic force microscope (AFM) image of the SWNT rope. Bulk laser-grown material with average tube diameter ~1.4 nm was dispersed in ethanol and then dropped onto a substrate consisting of degenerately-doped Si with 100 nm oxide. Using AFM we selected a 35-nm diameter rope, over which a pattern of chrome-gold leads was defined by electron-beam lithography and liftoff. A fifth contact to the substrate functioned as a metallic back gate.[13] Copper wires were attached to the substrate, the assembly was inserted into a pyrex tube, and the end around the wires sealed with epoxy. Into the other end was vacuum-distilled a few mg of K metal. After sealing, helium was diffused into the tube to afford good heat transfer at low temperatures. After completing the pristine measurements, K doping was carried out by heating the sample at 423 K (limited by the epoxy) and the metal reservoir at ~400 K, for 15 h. Bulk mats were also doped in sealed glass tubes at higher temperatures, then transferred in a glove box to the sample holder of a closed-cycle refrigerator. The weight uptake of the mats corresponded to KC_{8-10}, the saturation limit for graphite and C_{60}.

Figure 2(a) compares the $R(T)$ behavior of the pristine rope and a bulk mat of similar material. Both exhibit weakly metallic behavior at high T, a crossover temperature T^* below which dR/dT becomes negative, and a diverging resis-

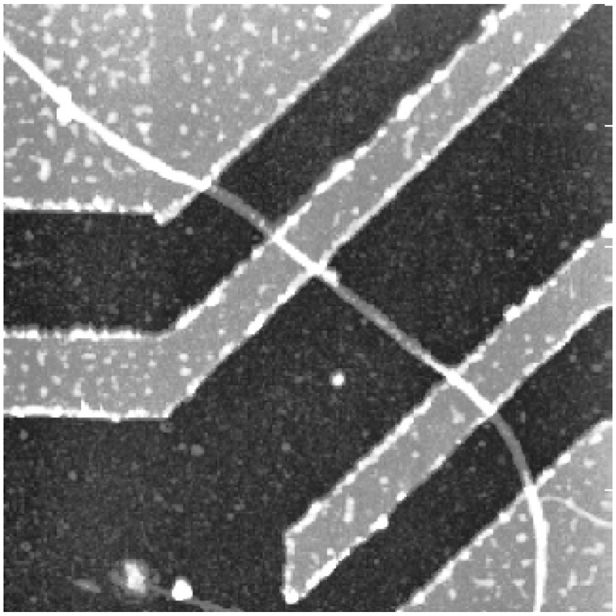

FIG. 1. AFM image of a ~35 nm SWNT rope on oxidized Si, over which are deposited four chrome-gold leads (spacing between voltage probes 1.4 μm).

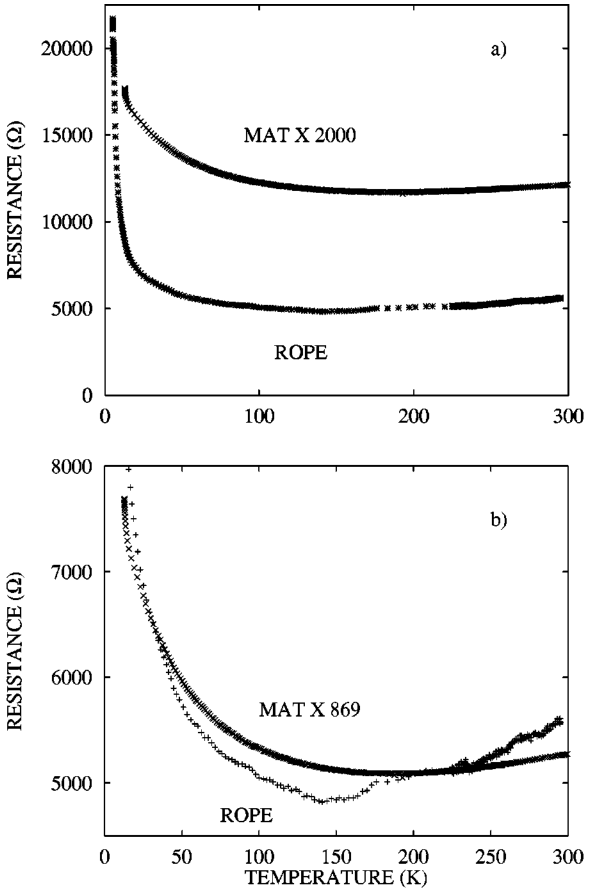

FIG. 2. Four-point resistance vs temperature for a pristine rope and for a mat of similar material. (a) Full range of measured R with the mat data multiplied by 2000 $[R(\mathrm{rope}) \gg R(\mathrm{mat})]$. (b) Same data normalized at 200 K and plotted on an expanded R scale to emphasize the similar T dependence above 13 K.

tance as $T \rightarrow 0$.[14] The common qualitative behavior suggests that the features observed in mats are intrinsic to the ropes of which the mat is comprised.

To further compare the bulk and single-rope behavior, resistivities were estimated from sample dimensions. Two values were calculated for the mat: ρ_{macro} based on the actual thickness and ρ_{micro} using an effective thickness inferred from the sample length, width, and mass, and the density of an ideal rope. We find that $\rho_{macro} \sim 20 \rho_{micro}$, which we attribute to the empty volume associated with a large density deficit/porosity.[12,6] More interestingly, ρ_{micro} is only 20 times larger than ρ_{rope}. The large-scale conduction path in mats includes many ropes, so ρ_{micro} is expected to include an important contribution from the resistance of inter-rope contacts. These are generally believed to involve temperature-dependent tunneling through potential barriers. In fact, the (scaled) temperature dependences of R(mat) and R(rope) are identical within 10% from 13 to 300 K, as shown in Fig. 2(b). Thus, rope-rope contacts might increase the absolute value of R(mat) but have little effect on its temperature dependence above 13 K. Another possibility is that the actual length of the tortuous path through many ropes in a mat is much longer than the voltage probe separation (the factor of 20 found above seems reasonable), and that the rope-rope contact resistance has little or no effect. The situation at lower T needs to be clarified by more complete data for both kinds of sample. Several authors have demonstrated that R(mat) vs T can be fit below 5 K to variable range hopping models.[15–17]

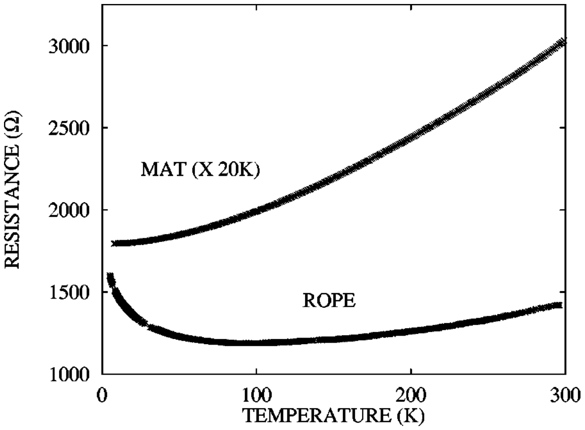

FIG. 3. Four-point resistance vs temperature for the rope and mat samples in Fig. 2, after doping with potassium. The mat data is multiplied by 20 000.

Similar data after doping are shown in Fig. 3. Both the mat and the rope show an overall decrease in R with doping, and little change in the positive dR/dT slope at high T. The divergence in R(mat) as $T \rightarrow 0$, as well as the weakly negative dR/dT regime between ~ 13 K and T^*, are completely suppressed by doping. Both effects are less dramatic in the rope, for which the divergence is not completely suppressed and T^* moves down from 150 to 100 K. These differences in doping response of mats and ropes could be attributed to incomplete doping of the latter.[18] Another likely explanation is that not all ropes contain the same admixture of metallic and semiconducting tubes, so one expects some dispersion in the doping response of individual ropes which is averaged out in mats. The important observations are twofold. First, conduction in both ropes and mats is enhanced by doping, a qualitative indication that previous results on doped mats[7,8] reflect charge transfer[19] rather than improvement in rope-rope contacts or other morphological effects. Second, the doping-induced suppression of the divergence is intrinsic since it occurs in both ropes and mats, a fact which must be accounted for in a viable explanation of its origin.

Finally, we examine the effects of electrostatic modulation on G (differential conductance dI/dV at small bias) of the same rope described above, in both the pristine and doped states. Figure 4 shows G (4-probe) vs back gate voltage V_g, measured at 5.3 K. Overall, G of the pristine rope decreases with increasing V_g by a factor of ~ 2 over the ± 10 V range; this rope behaves like a poor p-channel FET in parallel with a V_g-independent conductor. Superposed on this behavior are oscillations of order 10–20 % with ~ 2 V spacing. Both the FET behavior and the oscillations are eliminated by potassium doping, while $G(0)$ is enhanced by a factor ~ 20 consistent with Figs. 2 and 3.

Interpreting Fig. 4 requires an estimate of the ''lever arm'' dE_F/dV_g, which connects modulations of E_F and V_g. This depends on the capacitance between backgate and the object being modulated (in particular the diameter of a tube or rope) and on the density of states $N(E)$, among other things.[13] While difficult to obtain a quantitative estimate, it is

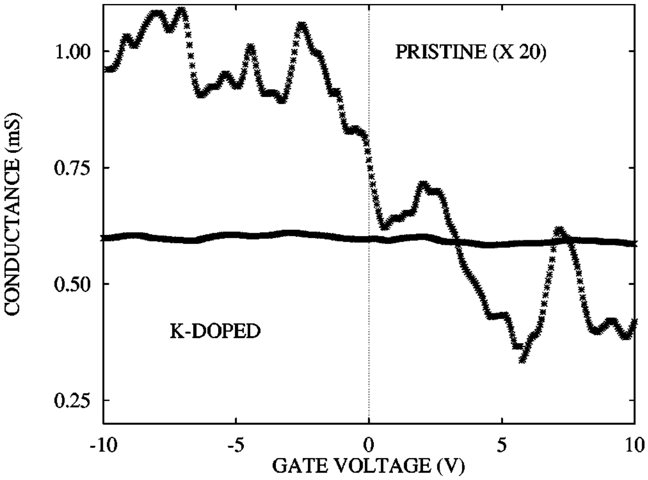

FIG. 4. Conductance versus gate voltage for pristine and K-doped rope at 5.3 K, averaged over ~ 100 sweeps. The rope is the same as in Figs. 2 and 3. The oscillations are completely reproducible.

certainly true that the lever arm will be largest for a semiconducting tube and smallest for a metallic rope. Our crude estimates for a rope comprised of 400 metallic tubes range from 8 to 160 meV depending on assumptions about charge uniformity. Intrinsic semiconducting tubes $[E_F(0)=0]$ would increase this range, while other effects such as charge inhomogeneity, auto-doping (see below) and E_F pinning by the metal contacts[10] would decrease it. In any event, our range of V_g is too small to shift E_F between metallic subbands or across semiconducting gaps. On the other hand, chemical doping with $\sim 0.1e$ transferred per C atom should move E_F by almost 2 eV.[20]

Armed with the above, we can now compare the Fig. 4 data with various models. We begin with the overall behavior before and after doping. It has been suggested[21] that tube-tube interactions open a ~ 0.1 eV pseudogap at E_F. If the rope were initially intrinsic [that is, $E_F(0)=0$ for both semiconducting and metallic constituents], finite V_g of either sign would (at best) shift E_F into a higher $N(E)$ region and G would increase symmetrically about $V_g=0$. This disagrees with the observed steplike *p*-type behavior. A second model assumes that $E_F(0)$ of the ‘‘pristine’’ rope is not at midgap but is shifted downward by ~ 0.3 eV into the valence band of at least some of the semiconducting tubes, as previously observed in single-tube experiments.[10,11] Positive V_g would deplete these tubes, switching them off. This model thus predicts two plateaus in $G(V_g)$—at large negative V_g all the semiconducting tubes conduct (as well as the metallic ones) and G is high, while at large positive V_g only the metallic tubes conduct and G is lower. At still larger positive V_g we might expect G to again increase as E_F enters the conduction band of semiconducting tubes, but this level of electrostatic doping has so far been unattainable, even in single tubes. The observed two-plateau behavior is consistent with the ‘‘pristine’’ curve in Fig. 4, and is even more pronounced in other ropes.[13]

This second model also explains the effect of doping on $G(V_g)$. After *n*-doping with potassium, $G(V_g)$ is featureless and 20 times greater than $G(0)$ before doping. E_F of the doped rope is now far from any band edges; all the tubes become *n*-type metals when K-doped, eliminating the *p*-type behavior. Furthermore, doping should move E_F to an energy where $N(E)$ is higher than in the pristine case, increasing G *and* reducing the lever arm such that G becomes featureless. In addition, the doped system is probably more three-dimensional than the undoped one, which would tend to damp out singularities in $N(E)$ at band edges.

Two ideas have been proposed to explain the *p*-type behavior of ‘‘pristine’’ semiconducting tubes. Tans *et al.*[10] proposed that the metal leads pin E_F at the valence-band edges, creating a barrier to hole transport. In large ropes this effect should be significantly reduced by the longer distance between contacts and by more efficient screening. Alternatively, Martel *et al.*[11] proposed that tubes are inadvertently doped during processing, such that variations in G with V_g reflect electron depetion at $V_g=0$. Our interpretation of the rope data is consistent with the second idea; semiconducting tubes in our rope are initially strongly *p* type. This is also consistent with bulk thermopower data, which shows evidence for *p*-type metallic conduction down to low temperatures.[22] There have been reports that ‘‘pristine’’ samples are actually (reversibly) *p*-doped in air.[23–25] A similar effect occurs in solid C_{60}.[26]

The weak oscillations in $G(V_g)$ before K doping are harder to explain. We offer two possibilities and rule out a third, all resting on the fact that semiconducting tubes in a rope will have slightly different diameters and chiralities. First, we envision small gaps (<0.1 eV) at the crossing points between different semiconducting bands, induced by intertube interactions. Tuning E_F through these minigaps would produce oscillations superposed on the overall decrease in G due to carrier depletion. Alternatively, defect states induced in semiconducting tubes by unintentional doping or structural defects could introduce localized states in the semiconducting gaps. These could also perturb the extended state spectrum, both effects leading to G modulation as E_F is tuned through them via V_g. Finally, if intertube interactions were negligible we would expect to observe a superposition of the $G(V_g)$ behavior of all the constituent tubes. However, since single tubes show a monotonic decrease in G with V_g,[10,11] crossing successive valence-band edges would lead to a steplike decrease in G rather than the observed oscillations.

We have shown that the temperature dependent resistance of a rope is essentially the same as that of a bulk mat of similar material above 13 K, and that the difference in absolute resistivies can be attributed to the longer effective rope path length in the mat (i.e., without invoking rope-rope contact effects). The crossover at T^* from positive to negative dR/dT in *undoped* mats and ropes can be fit with a polymer-like model of defect-induced intertube hopping,[27] while applying the same model to *doped* materials would imply a *decrease* in defect density. The strong divergence in R as $T \rightarrow 0$ is also common to our rope and mat, indicating that it is an intrinsic feature. K doping the rope and the mat leads to similar effects; an overall decrease in R and supression of the low-T divergence. Along with the doping-induced change in V_g characteristics, this proves that chemical doping is a charge transfer process (as in similar carbon hosts) rather than a change in rope-rope contact properties. The V_g characteristics of the ‘‘pristine’’ rope support the idea that

SWNT materials are inherently *p*-type due to tube-level defects or inadvertent doping by exposure to air.

Important contributions to this work were made by R. Antonov and Z. Benes, and we acknowledge helpful discussions with E. J. Mele, C. L. Kane, and A. Maarouf. Nanotube samples were graciously provided by the Rice group. Supported by DOE DEFG02-98ER45701 (R.S.L., H.J.K., J.E.F., J.H.), NSF DMR98-02560 (J.H., M.R., A.T.J.), Fonds FCAR Québec (J.L.) and the Packard Foundation (J.L., A.T.J.).

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[14] The divergence in our mat data is less dramatic than for the rope since the former was measured only down to 13 K. Other mat data extending to the mK range show several more decades of increasing R as $T\rightarrow 0$ (Refs. 15–17).

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[18] The rope may not be K doped to saturation since we were forced to dope it at lower T due to the epoxy seals. Indeed the doping-induced reduction in $R(300\ \mathrm{K})$ is only a factor 4 compared to 40 for the KC8 mat.

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