Pressure dependence of the resistivity of single-wall carbon nanotube ropes

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We have performed dc transport measurements on purified thick films of single-walled carbon nanotubes under hydrostatic pressures up to 2 GPa in the temperature range 4–300 K. At room temperature we have found nonmonotonic variation of the resistance with applied pressure. The resistance first drops with increasing pressure, but in the range where hexagonal deformation of the tubes is evidenced by the Raman experiments of Venkateswaran *et al.* [Phys. Rev. B **59**, 10 928 (1999)], we see a fast increase in sample resistivity acompanied by very long time-scale relaxations. The temperature dependence of the resistivity does not change much with pressure, and we find an $\exp[(T_0/T)^{1/4}]$ temperature dependence indicating hoppinglike conduction.

Charge transport studies on carbon nanotubes revealed up to now the most fascinating information about the electronic properties of these mesoscopic objects. Findings include weak localization, Aharonov-Bohm oscillations,[1] and indications of Luttinger-liquid behavior.[2] These experiments have been carried out on either multiwalled nanotubes or ropes of single-walled carbon nanotubes; in the latter case assuming that transport in a single rope is dominated by a single metallic tube reaching from one end to the other and that the interaction between strands is electrostatic.

The single-walled carbon nanotube is a very attractive system since so far it seems to be the best realization of a one-dimensional metal. Nevertheless, the temperature dependence of the resistivity of individual nanotube ropes deposited on a substrate is in most of the cases nonmetallic. It is known that torsions, twists, and interaction with the substrate can all induce important local deformations which influence the electronic properties. These interactions seem to be partially absent in mats of nanotubes: one indication of this might be that in nanotube mats the temperature dependence of the resistivity is metallic above a characteristic temperature T^*. This crossover temperature depends on the number of the charge carriers on the tubes: e.g., in potassium doped mats T^* shifts to low temperatures, while in high-temperature annealed samples (believed to be the pristine sample) it is in the 400 K range.[3]

In a recent Raman-scattering measurement it was found that single-walled carbon nanotube (SWNT) ropes are sensitive not only to the above-mentioned deformations but to hydrostatic pressure as well.[4] The radial breathing mode has disappeared above a pressure of 1.5 GPa indicating the loss of the cylindrical shape of the nanotube cross section due to hexagonal deformation. In this paper we have addressed the effect of this deformation on the electronic properties measured through the dc resistivity of a pristine single-wall carbon nanotube mat.

We have prepared SWNT's by arc discharge under a 500 mbar He atmosphere using a 20 mm pure graphite cathode and a 5 mm anode with a 3 mm hole filled with a mixture of graphite, Ni, and Y in 2:1:1 mass proportions.[5] The voltage and current used were approximately 25 V and 100 A. The raw soot was sonicated at room temperature with concentrated nitric acid for a few minutes then refluxed for 4–6 h. After this cooling water was added to get a $6M$ HNO_3 solution, which was left for the next 8–12 h. The solution was centrifuged several times and the supernatant rejected until the pH of the solution was around 6.5. This solution contained mostly SWNT ropes with a small amount of carbon coated metallic particles. Surfactant was added to the solution and left undisturbed for 3–5 days in order to get some aggregation of nanotubes after which the solution was filtered with a 1 μm pore size filter. This has produced a self-sustaining buckypaper which was used in these experiments. Part of this paper was subject to an additional heat treatment in vacuum at 1200 °C. The reason for doing this treatment was to get rid of nitric acid that may intercalate the ropes during the purification and act as a dopant.[6]

Chips of typical size of 3 mm by 0.2 mm were cut and mounted in a piston-type cell for dc resistance measurements. We used kerosene as the pressure transmitting medium. The pressure was measured with an InSb single crystal manometer placed next to the sample. We have noticed some pressure loss upon cooldown, typically 0.2 GPa.

Figure 1 shows the temperature dependence of the resistivity of an ''as made'' and a heat treated buckypaper. The ''as made'' sample has metal-like temperature dependence down to about 150 K (T^*) and from there the resistance rises with decreasing temperature. The heat treatment increases the room-temperature resistivity by about a factor of 5 and pushes the T^* temperature higher, to about 350 K. The room-temperature conductivity of the heat treated sample is about $20\ \Omega^{-1}\,\mathrm{cm}^{-1}$, however, since buckypaper is a porous material with uncontrolled compactness this value is only indicative. The change in resistivity and the shift of the minimum can be naturally explained if we note that the sample consists of ropes, themselves containing strands of metallic and semiconducting tubes loosely touching each other through semiconducting tubes or/and through amorphous carbon not eliminated by the purification. In this picture the resistivity minimum is the result of a metallic on-tube conduction in series with an activated, hoppinglike conduction of the contact regions. Doping will enhance the conductivity of the semiconducting contact regions as well as doping semiconducting tubes in the ropes. Once the contact regions become better at conducting, we pick up more from the temperature dependence of the intrinsic, on-tube conductivity.

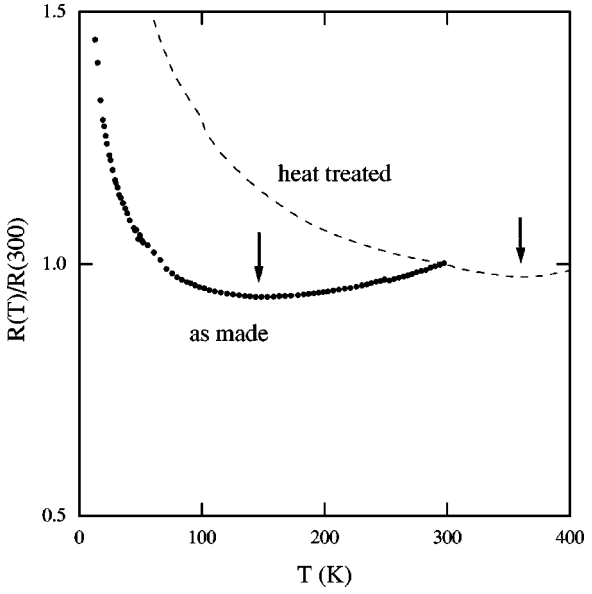

FIG. 1. Temperature dependence of the resistivity of a chemically purified and filtered buckypaper and one that received an additional heat treatment in vacuum at 1200 °C. One can note the shift of the minimum of the resistivity, T^* to higher temperature. Upon the heat treatment sample resistivity has increased by a factor of 5.

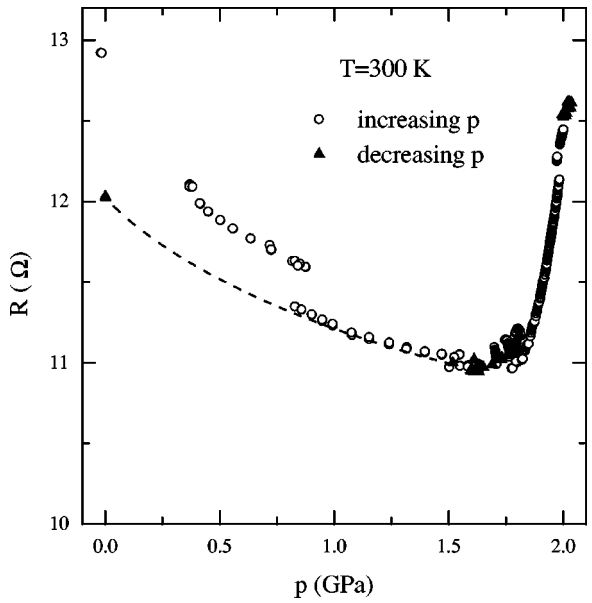

FIG. 2. Pressure dependence of the room temperature resistivity. Circles are points taken upon increasing pressure, triangles upon decreasing. Upon increasing the pressure we have made $R(T)$ measurements at 0.8, 1.5, 1.8, and 2 GPa. The discontinuity in the curve at 0.8 GPa is due to this interruption and we think that it reflects the annealing of the sample.

This is evidenced by our simultaneous dc and optical conductivity measurements on pristine and K-doped buckypaper where we have found metallic optical conductivity even in heat-treated samples despite a nonmetallic dc resistivity, furthermore, we have found that $\sigma(\omega \rightarrow 0)$ only increases a factor of 3 upon doping while σ_{DC} changes by one order of magnitude.[3]

Figure 2 shows the pressure dependence of the room-temperature resistivity. Upon increasing the pressure up to 1.5 GPa the resistance drops by about 10% and reaches a shallow minimum. Between 1.5–1.8 GPa we see interesting relaxational phenomena about which we will talk later. Increasing the pressure further, the resistance rises sharply and keeps this tendency up to the highest pressure we could reach, 2 GPa. Upon lowering the pressure resistivity changes are reversible down to about 1.5 GPa.

Similar experiments have been carried out by Bozhko *et al.*[7] however they only saw an increase of R between 1 and 3 GPa with p during their first pressure cycle, on subsequent runs dR/dT was always negative. We think that this can have several causes: (i) owing to their apparatus, their pressure is only quasihydrostatic, (ii) they induce irreversible changes in their sample indicated by the 2–4 times increase of sample resistance after the first pressure cycle.

We assign the initial decrease of the resistivity to compacting the buckypaper thus improving rope-rope contact. This change is partially irreversible: after the pressure cycle the sample resistance has decreased by about 8%. Above 1.8 GPa the resistivity increases steeply with pressure and a more striking feature is the reproducibility of this change upon decreasing pressure. This indicates that it is not due to rope contacts breaking up but rather some intrinsic change of the on-tube conductivity. The source of this sudden change might be found in a recent experiment by Venkateswaran *et al.*[4]. They have found that hydrostatic pressures above 1.5 GPa suppress the Raman-active radial breathing, and greatly reduce the tangential modes of SWNT bundles. They attributed these changes to the hexagonal deformation of the tubes in the bundle due to compression. This change in the symmetry of the tubes could lead to the aforementioned changes in the transport properties., e.g., opening of a gap in the metallic tubes or increasing the probability of umklapp processes[8].

Long time-scale relaxation in this pressure range shows that the induced rearrangements are not instantaneous. Figure 3 shows the sample resistance and the pressure as a function of time between 1.5–1.8 GPa. Arrows indicate the instances when the applied pressure was increased. The sample resistance relaxes on very long time scales (>1 min) in this pressure range. This type of behavior was not present in other pressure ranges. The first and most obvious idea that comes to mind in order to explain this phenomenon is changes in the sample temperature. However, the sample has $dR/dT<0$ so the temperature should increase during the relaxation which implies that it must have decreased upon compression which, however, is not possible. Thus we think that this is a manifestation of a slow movement of the deformed SWNT within the rope towards a new equilibrium position.

Figure 4 shows the sample resistance as a function of temperature, measured at different pressures up to 2 GPa. $dR/dT<0$ for all the pressures indicating that the transport is limited by the tube-tube contact regions. We did not see any change in the sign of dR/dT, unlike Bozhko *et al.*[7] however we must stress that while their sample had $dR/dT>0$ at room temperature and changed sign to nonmetallic at about 2 GPa, our sample was semiconducting at ambient pressure. We think that the change in dR/dT is again a manifestation

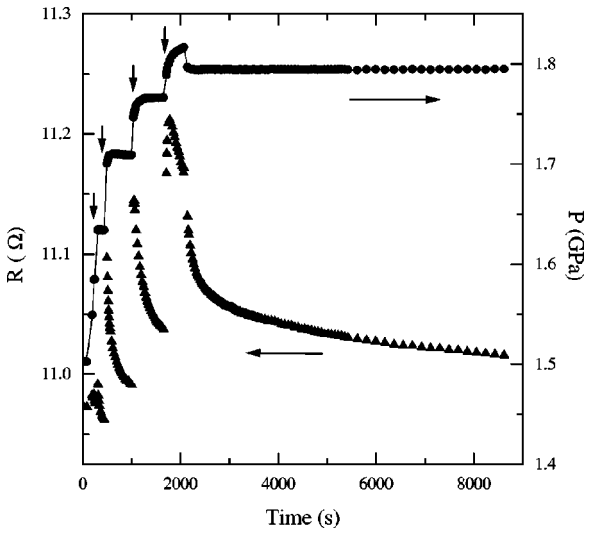

FIG. 3. Relaxation of resistance in the 1.5–1.8 GPa pressure range. The right-hand scale shows the pressure, the left-hand scale the sample resistance as a function of time. Arrows indicate where pressure was raised.

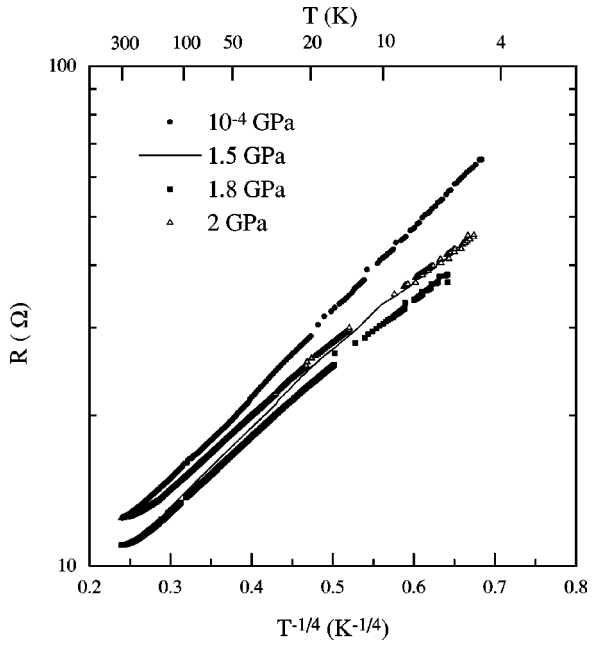

FIG. 4. Temperature dependence of the resistivity measured at different hydrostatic pressures. Plots show $\log(R)$ as a function of $T^{-1/4}$ in order to demonstrate hoppinglike conduction.

of irreversible changes caused during the first pressure cycle. This is absent in our case, probably because of the more limited pressure range.

In Fig. 4 we have plotted the logarithm of the resistance vs $T^{-1/4}$ in order to demonstrate that the temperature dependence of our curves suggest a hoppinglike conduction, similar to the findings of others.[9,10] Since the change in resistivity is less than one order of magnitude between 4 and 300 K, the slope of the curves is rather small giving a characteristic temperature T_0 in the neighborhood of 150 K, a value too low to apply the variable range hopping formula to directly. Furthermore, the temperatures where the $T^{-1/4}$ dependence is observed is too high to apply the single phonon assisted hopping model of Miller and Abrahams.[11] There is an extension of this model proposed by Emin[12] which exactly includes multiphonon contributions which gives $lg(\sigma) \propto (T_0/T)^{1/4}$ at temperatures higher than found for the single phonon model. In this model, the characteristic temperature T_0 only depends on the electron-phonon coupling constant and the phonon population. If we apply this model the small change of the slope with applied pressure can be due to the stiffening of the lattice under compression and lowering the phonon population at a given temperature. Nevertheless, even if we think seriously to apply this picture to the assembly of the SWNT mat, one would expect a much stronger temperature dependence of the resistivity than observed.

In our opinion a more realistic model would be the thermal fluctuation assisted hopping model of Sheng,[13] which was elaborated for incoherent charge transport between macroscopic metallic objects. In this model thermal fluctuations of the Fermi level of the objects help the hopping of electrons through the sample. The verification of the applicability of this model would need resistivity measurements down to very low temperature and detailed *I-V* characteristics. This is beyond the scope of the present paper and will be the subject of future studies.

In conclusion, we have performed dc resistivity measurements on buckypaper under hydrostatic pressure in the 4–300 K temperature range. We have found nonmonotonic variation of the room-temperature conductivity with pressure along with some resistivity relaxation in the pressure range where Raman spectra are shown to change drastically. We attribute these changes to two things: to compacting the mat which happens at low pressures, and to a reversible deformation of the tubes at higher pressures. The temperature dependence of the conductivity indicates hopping conduction in the whole range of applied pressure.

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