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Potassium Doped Single Wall Carbon Nanotubes: Resistance under Pressure

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We report *in situ* measurements of four-probe dc resistance (R) of K-doped purified single wall carbon nanotube (SWNT) "buckypaper" as a function of quasi-hydrostatic pressure. Doped samples show completely different behavior compared to that of pristine nanotubes in the pressure range up to 90 kbar. The characteristic increase in the resistance of pristine buckypaper above 10 kbar, associated with the formation of kinks or/and twists of tubes, is not observed in K-doped samples. This may originate from 1) a substantial change in electronic band structure of donor intercalated nanotubes, 2) completely different transport properties of defect structures, or 3) higher stiffness of doped SWNT's which prevents formation of kinks and twists in this pressure range. On deintercalation, the pristine behavior of $R(P)$ is restored, establishing the reversibility of potassium vapor-transport doping.

Keywords: carbon nanotubes; transport properties; deformations; high pressure; potassium; intercalation

INTRODUCTION

Carbon nanotubes have received much attention due to their structural stability and novel electronic properties. Single-walled carbon nanotubes (SWNT), prepared by metal-catalysed laser ablation of graphite, form close-packed bundles or "ropes" of ~14 Å diameter tubes packed in a two-dimensional triangular close-packed lattice[1]. High purity samples containing a substantial

fraction of metallic and small-gap tubes exhibit overall metallic behavior in which the resistivity increases approximately linearly with increasing T over a wide temperature range. This is understood in terms of the coupling between conduction electrons and long wavelength twistons, i.e. torsional shape fluctuations[2].

SWNT can be doped with either donors (alkali metals) or acceptors (Br_2, I_2, HNO_3 etc.)[3,4]. On doping, the dc resistivity decreases by a factor of ~30-50, and the metallic behavior (i.e. $dR/dT>0$) is extended to lower temperatures[3].

Electrical transport and other physical properties of ropes may be significantly affected by tube-tube interactions. Thus the application of high pressure may help in understanding electronic or mechanical phenomena. Recently we have shown that quasi-hydrostatic (with no fluid) compression of purified, unoriented, highly crystalline single-wall carbon nanotube material reveals an exceptionally large and reversible volume reduction[5]. We suggested that this originates from the crushing and flattening of tangled ropes of, changing the tube cross-section from circular to elliptical.

Recent investigations of pressure-dependent Raman-active vibrational modes[6] showed that the radial mode intensity disappears beyond 15 kbar, this is attributed to a loss in the electronic resonance due to a distortion of the cylindrical cross section under compression.

Here we present *in situ* four probe dc resistance *vs.* pressure of pristine and potassium doped SWNT buckypaper up to 90 kbar.

EXPERIMENTAL

Purified single wall carbon nanotubes were synthesized by double laser ablation of metal-doped graphite targets, graciously provided by the Rice University group. These exhibit a diameter distribution peaked around 13.6 Å, close to that of a (10,10) nanotube. The tubes are packed in a 2D triangular close-packed lattice, with inter-tube spacing 3.4 Å typical of van der Waals interactions.

Potassium doping was carried out by vapor transport. A Pyrex tube with SWNT strips and excess K metal at the opposite end was evacuated, sealed and heated to 270°C (with a small temperature gradient to avoid coating the sample with metal) for 20 hours. As for graphite, this method produces a saturation composition ~ KC_8[3].

Four-probe dc resistance R *vs.* pressure P up to 90 kbar was performed under quasi hydrostatic conditions in a Bridgman-type anvil apparatus. We used rectangular 2×6mm SWNT strips (2 mm between the potential contacts). Doped samples were transferred in an argon glove box into Teflon ampoules with provision for airtight contacts. The ampoule was sealed by pressurization and placed in the high pressure assembly (details can be found elsewhere[7]).

RESULTS AND DISCUSSION

Figure1[a] presents $R(P)$ at 300 K of the pristine SWNT buckypaper used later for K doping. $R(P)$ is reproducible for different samples from the same batch, whereas $R(P)$ changes substantially from the first to subsequent cycles on the same sample. The main feature that we would like to point out is that above 8-10 kbar, R starts to increase with pressure. Moreover, we find in separate experiments at ~10 kbar that the temperature coefficient of resistance (TCR) irreversibly changes sign, from positive to negative. This $R(P)$ behavior is characteristic for the first cycle only, and therefore represents some irreversible process - formation of kinks, local flattening or even crushing of tubes at contact points between ropes or rope bundles. A.Rochefort[8] showed that bending of nanotubes decreases their transmission function $T(E)$ which represents the sum of the transmission probabilities over all contributing conduction channels, leading to an increase in R. The effect is particularly strong at bending angles higher than 45° when the strain is sufficient to produce kinks in the nanotube structure. These are expected to scatter the conduction electrons at the deformed regions leading to carrier localization. The reduction

in transmission function is correlated with significant *s-p* hybridization due to the increased curvature produced by bending.

These kink deformations appear to be irreversible after pressure release - IR investigations of high pressure treated nanotubes[9] showed 2-3 fold splitting of 1520 and 1020-1050 cm^{-1} bands. Splitting may reflect the local redistribution of electronic density in the aromatic structure of nanotube walls, i.e. a more pronounced sp^2-sp^3 character.

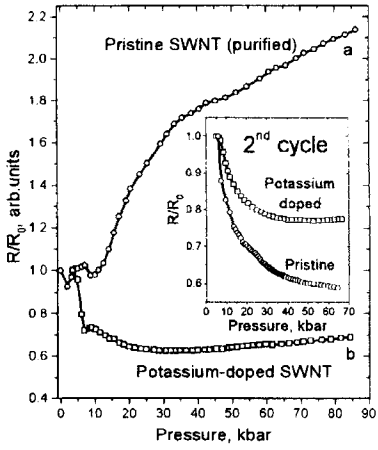

Figure 1. 4-probe dc resistance versus pressure of pristine (circles) and potassium doped (rectangles) SWNT buckypaper. The inset shows the second cycle *R(P)* dependence for the same samples.

Another candidate for the irreversible transport property modification is pressure induced twisting of the tubes. Normally, metallic armchair nanotubes develop a band-gap which initially scales linearly with twisting angle and then reaches a constant value[10]. This saturation is associated with a transition to a flattened helical structure. Extended Hückel calculations[10] show that twisting leads to drastic modification of the electrical properties of nanotubes - for twisting angles larger than $2°nm^{-1}$, the transmission that determines the linear conductance of the system decreases exponentially. Already a twist of $4°nm^{-1}$ reduces the transmission by a factor of 14, at $8°nm^{-1}$, $T(E_F)$ has been decreased by more than 2 orders of magnitude, and considering transport into a strongly twisted, helical shape nanotube, the decrease in $T(E)$ is expected to be about 5 orders of magnitude! Though the authors indicate that the energy required for even a moderate twisting of the tube is very large, the calculated energy deposited in the material by compression is sufficient for severe twisting even at moderate pressures.

Kinks or twists imposed by high pressure treatment into highly tangled network of tube bundles and ropes may be responsible for R increasing with pressure, as well as for TCR sign change at 8-10 kbar. Some of these defects remain after the first pressurization, leading to gradual and irreversible resistance increase on pressure release during the first run (by a factor of 5-10 from 90 kbar to ambient pressure) and reproducible graphite-like $R(P)$ behavior on the second (Fig.1 inset) and subsequent cycles. Moreover, these pressure imposed defects retain the negative nonlinear TCR slope at ambient pressure.

$R(P)$ behavior for potassium doped samples shows quite different behavior (Fig 1[b]). By 10 kbar, R of doped samples drops by 40%. A similar abrupt decrease in $R(P)$, but greater by an order of magnitude, is found in the unpurified (~70% SWNT) material, which we associated with the compaction which improves the number and density of contacts between ropes[7]. From 10 to 45 kbar the K-SWNTs resistance decreases gradually with pressure, contrary to that of pristine nanotubes (Fig. 1[b]). At still higher pressures, $R(P)$ increases slightly (by 2% from 45 to 90 kbar). The second cycle (Fig.1 inset) reveals only a gradual decreasing $R(P)$ by ~20% up to 65 kbar. Similar behavior but with an overall 100% decrease was found for the second cycle of pristine material.

Two possible explanations of the weaker $R(P)$ dependence of K-doped nanotubes are as follows. It may be due to substantial modification of the electronic band structure, leading to qualitatively different effects at kinks and twists. The second possibility is that buckypaper becomes stiffer on doping, reducing the likelihood of kink or twist formation.

After exposing K-doped samples to air, $R(P)$ is exactly restored to the behavior of pristine material, proving that potassium vapor-transport doping is reversible.

CONCLUSION

In situ measurements of four probe dc resistance *vs.* pressure of potassium

doped single wall carbon nanotubes show completely different behavior compared to that of pristine nanotubes in the pressure range up to 90 kbar. The characteristic increase in the resistance of pristine buckypaper above 10 kbar, associated with the formation of kinks or/and twists of tubes, is not observed in K-doped samples. This may originate from a substantial change in the electronic band structure of donor intercalated nanotubes, completely different transport properties of defect structures, or from the higher stiffness of doped SWNT which prevents the formation of kinks and twists in this pressure range. Clearly, more measurements are needed to identify the mechanism of $R(P)$ behavior.

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