Transport Properties For Carbon Nanotubes Under Hydrostatic Pressure

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ABSTRACT

Multi-wall carbon nanotubes (MWNTs) were mixed with polystyrene (PS) by 20 wt%, which is slightly above the percolation threshold. Temperature (T) dependencies of Seebeck coefficient (S) and resistance (R) for the sample (MWNT-PS) were measured under hydrostatic pressure upto 1.2 GPa. The resistance at ambient pressure showed power law T-dependence ($R \propto T^{-\alpha}$) and agreed well with Luttinger liquid (LL) model. The exponent α agrees well with the theory prediction and the experimental data of 'bulk-contacted' single-wall carbon nanotube (SWNT). The α increases slightly under high pressure, suggesting enhanced influence of Coulomb interactions. This could be due to either an increased Coulomb screening length or a reduced Fermi velocity under high pressure. The pressure also increases S slightly. The small magnitude and linearity of S versus T shows that the metallic behavior is kept below 1.2 GPa. The theoretical prediction of pressure-induced metal-insulator transition for SWNTs was not observed. Experiments on SWNT mixed in polycarbonate (PC) is under way.

1 INTRODUCTION

The discovery of carbon nanotubes (CNTs) [1]–[4] had intrigued wide interests and researches in the past decade. The transport properties of single-wall carbon nanotubes (SWNTs) vary widely with the chirality (n_1, n_2) [5]–[8]. However, the nanotube chirality plays a much smaller role in the transport of MWNT due to the successive shells there [9]. In addition, because of the one-dimensional (1-D) nature of the CNT, Coulomb interactions can cause strong perturbations of the DOS near Fermi level even in the metallic states, results a Luttinger liquid (LL) [10], [11]. More interestingly, under high pressure, the calculation on (10, 10) SWNT predicted that the metallic CNT will transform into semiconducting phase when hydrostatic pressure was applied [12]. There have been experimental efforts to study SWNT under pressure[13], [14], which were not direct transport measurements. Thermal conductivity (κ) and Seebeck coefficient (S) were measured for single multi-wall carbon nanotube (MWNT) [15]. However, measurement of transport properties under high pressure is very difficult, especially for thermoelectric properties. So far there were only successful measurements on SWNT buckypaper and mats [16], [17]. It is known that for all the polycrystalline samples, S is insensitive to sample size, non-conducting impurities that located between grains. Thus we expect the measurement of S for the MWNT mixed with polystyrene (MWNT-PS) reflects the intrinsic thermoelectric properties of MWNT. In this paper, we report our measurement of both the resistance (R) and S of MWNT-PS under hydrostatic pressure up to 1.2 GPa.

2 EXPERIMENTAL DETAILS

Twenty weight percent of commercial MWNT from Hyperion Catalysis were machine mixed in polystyrene. This weight percent was chosen to ensure percolation transport in the mixture [18]. The diameters of the MWNTs typically ranges from 50 nm to 200 nm, the length of the bundle is about 1–10 μm.

The hydrostatic pressure was generated inside a Teflon cup housed in a Be-Cu high pressure clamp [19]. The 3M Fluorinert was used as the pressure medium in order to get *hydrostatic* pressure. The pressure was calculated by the force over area at room temperature. Our previous experiments used superconducting Pb as a manometer to measure pressure near liquid helium temperature and demonstrated that the pressure obtained using this method is within 10% throughout the temperature range 4 K to 300 K [20].

The resistance was measured using dc four-probe method. The Seebeck coefficient under high pressure was measured using a very low frequency ac two-heater method [21]. Two surface mount resistors were driven by sinusoid currents that differ in phase by $\pi/2$.The amplitude of the currents can be adjusted to minimize the ac component of the base temperature fluctuation ($\tilde{T}$). The ratio ($\delta T/\tilde{T}$) of ac temperature gradient (δT) versus the base temperature fluctuation was monitored to ensure the correct and precise S from ac measurements [21]. Two pairs of T-type thermocouples were attached to the sample directly using EPO-TEC H20E silver epoxy and three independent signals were measured simultaneously to deduce the base temperature, temperature gradient and the Seebeck coefficient. The copper leads of the T-type thermocouples were calibrated relative to Pb using data from Roberts [22]. In this experiment, the sample size is about $1.5 \times 1.5 \times 3$ mm^3. Therefore, even with the surrounding of fairly good thermally conducting pressure medium, the measured Seebeck coefficient in the pressure cell at ambient pressure is in good agreement with that was measured outside. The small pressure effect on thermocouples were also considered and corrected.

3 RESULTS AND DISCUSSION

Figure 1 showed the resistance of our MWNT-PS sample under different pressure versus temperature (T). The pressure was increased from 0.0 GPa (A) to 0.30 GPa (B), 0.60 GPa (C), 0.90 GPa (D) till reached 1.20 GPa (E) then reduced to 0.50 GPa (F) and finally to 0.0 GPa (G). Although R decreases with increasing T, the data cannot be fit by an exponential law that describes a single band semiconductor. From the right side plot of figure 1, we can see that the R–T curve is largely reversible upon release the pressure, with the curve G only slightly higher than curve A.

The resistance at room temperature decreases with pressure significantly, which is an indication of a dominating role played by the inter-CNT coupling, although the weight percentage of CNT is above the expected percolation threshold.[18] Therefore, we did not expect the $R(T)$ observed being the intrinsic property of CNT. However, it turned out the R–T curves showed power law behavior and are very similar to the measurement of 'bulk-contacted' single SWNT [10] or 'end-contacted' MWNT [11].

The power law behavior of R–T dependence suggested that the LL-like resistivity is a very robust property of CNT. Indeed, one can argue phenomenologically that, the LL-like behavior is only related to the 1-D nature of the transportation and unlikely to be changed qualitatively by the existence of strong weak-links. Although detailed modeling on our MWNT-PS is definitely needed, we intent to take the R–T observed more seriously. In figure 2, we plotted the R–T curve in double logarithmic scale. All the curves under different pressures can be fit fairly well by the power law: $R \propto T^{-\alpha}$. The value $\alpha \approx 0.29$–0.49 under all the pressures, which agrees well with the theory prediction for CNT with Coulomb interactions [23]. This may suggest that the Luttinger liquid behavior for MWNT persists in our pressure range and that the Luttinger parameter $g \approx 0.18$–0.24. The slight increment of α under pressure indicates stronger influence of Coulomb interactions. This enhancement could be due to either increased Coulomb screening radius or reduced Fermi velocity under high

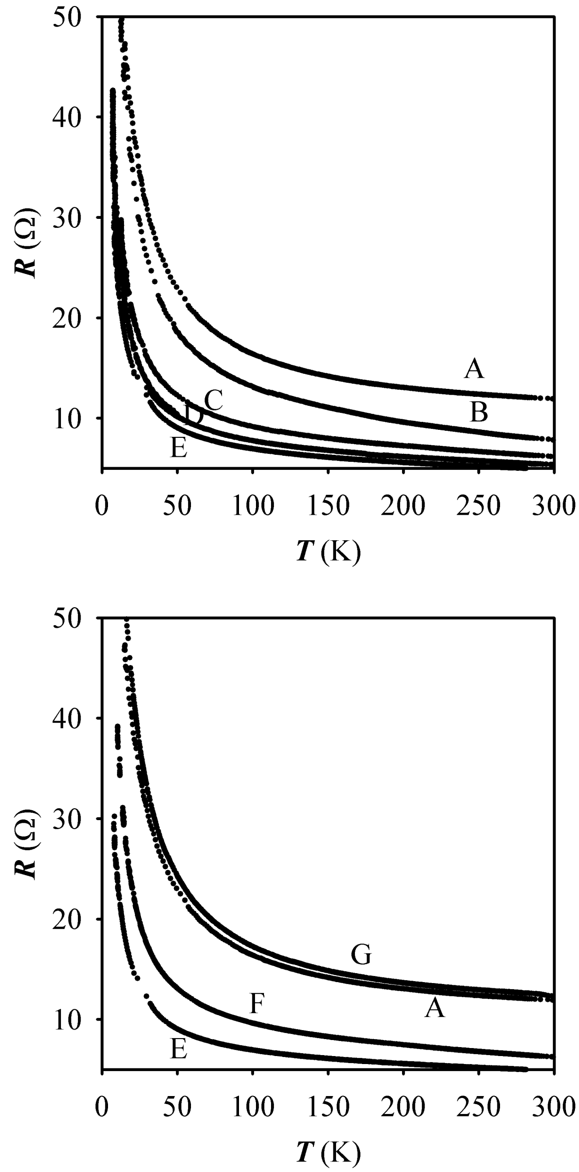

Figure 1: Resistance versus temperature for MWNT under different pressure. The pressure in GPa for each curve/point is A: 0.0, B: 0.30, C: 0.60, D: 0.90, E: 1.20, F: 0.50, G: 0.0 respectively. The upper graph shows the data for increasing pressure from 0 to 1.2 GPa; the lower graph shows the data for decreasing pressure from 1.2 GPa to 0. Curve A is repeated to show the reversible behavior of the resistivity.

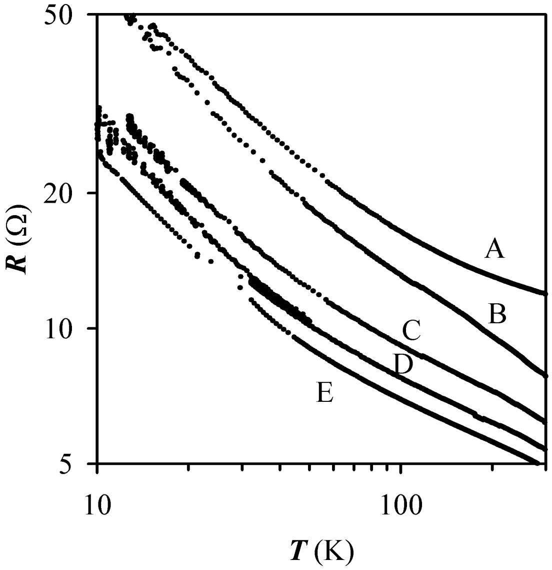

Figure 2: Resistance versus temperature for MWNT under different pressure plotted in double logarithmic scale. The pressure in GPa for each curve/point is A: 0.0, B: 0.30, C: 0.60, D: 0.90, E: 1.20 respectively.

pressure.

Figure 3 showed the Seebeck coefficient of our sample under high pressure. It showed small values and linear dependence of temperature, which is typical for the diffusion thermopower of metals. Upon applying pressure, S increases monotonically. Although the R measured here might be debatable, the S of MWNT-PS is based on both the multiband predictions and the experiences in polycrystalline samples with dominating grain boundary resistance. Compared with the data of single MWNT [15], our S value at room temperature is smaller, possibly due to the better conductance in bundled MWNT, the more prominent quantum confinement effects in single MWNT [24], or, more likely, the oxygen adsorption [25]. Apparently both Kim *et al*'s [15] and our MWNTs were "air-adopted".

Wu *et al* had calculated the (10,10) CNT under *hydrostatic* pressure [12]. They concluded that the tube will first be transformed into ellipse shape at 1.0 GPa, then finally transformed into peanut shape at 2.2 GPa. As a result, the metallic phase is transformed into semiconductor phase. The critical pressure is proportional to $1/r^3$, where r is the radius of the CNT at ambient pressure. We did not observe this phase transformation upto pressure of 1.2 GPa. High pressure upto 2 GPa was also applied to SWNT mats without any transport anomaly observed [17]. Although Sklovsky *et al* observed characteristic increase in the resistance for SWNT buckypaper [16], they explained the experiment results in terms of the formation of kinks or/and twists of tubes. Cur-

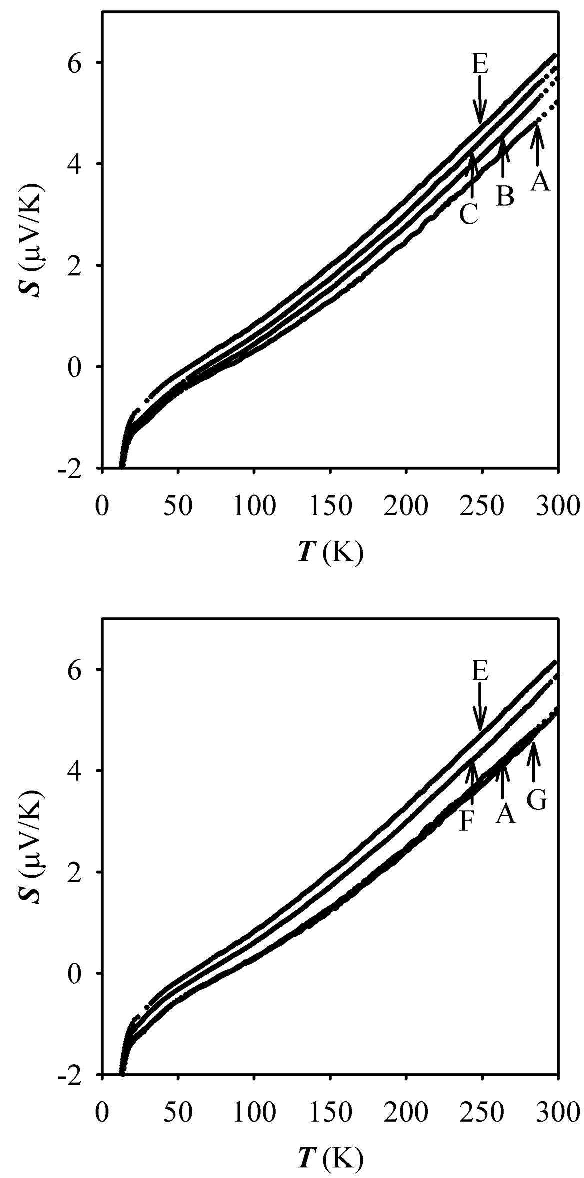

Figure 3: Seebeck coefficient versus temperature for MWNT under different pressure. The pressure in GPa for each curve/point is A: 0.0, B: 0.30, C: 0.60, E: 1.20, F: 0.50, G: 0.0 respectively. The upper graph shows the data for increasing pressure from 0 to 1.2 GPa; the lower graph shows the data for decreasing pressure from 1.2 GPa to 0. Curve A is repeated to show the reversible behavior of the resistivity.

rently we are working on SWNT-PC and single SWNT and MWNT under high pressure.

4 CONCLUSIONS

We measured the transport properties of SWNT mixed with polystyrene (MWNT-PS) under hydrostatic pressure. Our results were consistent with theories based on Luttinger liquid [8], [10], [23]. Our experiments suggested that the pressure enhanced the influence of Coulomb interactions. On the other hand, our experiments on MWNT did not see the metal-to-semiconductor phase transformation predicted by Wu *et al* for SWNT [12]. Further experiment on dispersed single SWNT with proper diameter is underway to verify this interesting theory.

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