The effect of annealing on the electrical and thermal transport properties of macroscopic bundles of long multi-wall carbon nanotubes

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Abstract

Electrical resistivity, thermal conductivity and thermoelectric power were measured on macroscopic bundles of long multi-wall carbon nanotubes (CNTs) in the temperature range between 2 and 300 K. While the electrical resistivity shows relatively small variation, the thermal conductivity is significantly enhanced and thermoelectric power changes sign from positive to negative after the samples are annealed in Ar at 2800 °C. Although the latter can be attributed to the adsorbed oxygen on the CNTs that is reduced through the annealing process, our results suggest the studied properties, especially thermal conductivity, are sensitive to the sample crystallinity that can be significantly improved by high-temperature annealing as well.

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Intense exploration of carbon nanotube (CNT) properties over the past decade has revealed a wide range of interesting thermal and electrical behavior. CNTs are theoretically predicted to have a large thermal conductivity due to their extremely long phonon mean free path \cite{1–3}. A room temperature value of over 3000 W/m K was reported in an individual multi-wall carbon nanotube (MWCNT) \cite{4}, suggesting that CNTs are a good candidate material for thermal management applications. Most thermal management applications require CNTs in bulk form such as fibers and sheets, where the tube-to-tube junctions can present substantial barriers to thermal transport. Recent advances in synthesis of vertically aligned CNT arrays resulted in a material that enables the study of bulk thermal properties in long macroscopic bundles of CNTs \cite{5}. However, previous studies have produced inconsistent results and interpretations of thermal properties. This is because the transport properties are extremely sensitive to the degree of crystallinity and defects/contamination in CNTs \cite{6,9–15}. The central issue is how to improve the crystallinity and purify CNTs, so that the intrinsic properties can be revealed. At present, whether the thermoelectric power (TEP) of CNTs has a positive sign is still an unsolved problem \cite{6,9–14}. While it is generally accepted that the positive TEP is the result of the presence of oxygen, the sign change of TEP has only been observed in single-wall CNTs \cite{6,9–13}. It is unclear whether MWCNTs have similar behavior, as both the electronic and phonon structures depend on the radius of the tubes and the inter-tube coupling. To gain further insight into the intrinsic properties of CNTs, we measured the electrical resistivity, thermal conductivity and TEP of long MWCNT bundles, extracted from vertically aligned arrays. These measurements demonstrate that the transport properties of MWCNTs can be altered by high-temperature annealing treatment.
The vertically aligned arrays of MWCNTs, shown in Fig. 1a, were grown using chemical vapor deposition [5]. After growth, the CNT bundles were detached from the mat with a razor blade, without applying high stress on the tubes. Standard four-probe measurements of the electrical resistivity, thermal conductivity and TEP were carried out using a physical property measurement system from quantum design. Electrical contacts to the CNT bundles of approximately 5 mm × 2.5 mm × 1.5 mm were made by first evaporating 1000 Å thick Au then attaching Cu wires using silver epoxy (see Fig. 1b). Both electrical current and heat flux were applied along the tube-alignment axis. To avoid sample variation between different growth runs, all samples are from the same mat, but treated after growth under different conditions. The measured samples include: (1) as-grown CNT bundles denoted as S1; (2) samples treated with pure methanol and annealed at 100 °C for 4 h (S2); (3) samples annealed at 1250 °C for 4 h (S3), and (4) samples annealed at 2800 °C for 4 h (S4). All annealing treatments were carried out in argon (Ar) atmosphere, and no attempt was made to avoid exposure to air after annealing. High-resolution transmission electron microscopy (HRTEM) images show that all samples consist of MW CNTs (see Figs. 1c and d).

Fig. 2a shows the temperature dependence of the electrical resistivity \( \rho \) for samples S1–S4 between 2 and 300 K. Note that all samples exhibit similar nonmetal-like behavior \( (d\rho/dT < 0) \) over the entire temperature range measured. At a fixed temperature, \( \rho \) decreases with increasing annealing temperature except for S3. To check whether this is caused by the errors involved in estimating the geometric factors \( L \) and \( A \) indicated in Fig. 1b, we use the room-temperature resistivity for each sample to normalize the data. Plotted in Fig. 2b is the temperature dependence of \( \rho/\rho(300\,\text{K}) \). It is obvious that the electrical resistivities of the annealed samples have stronger temperature dependence than that of the as-grown sample. Currently, there are two schools of thought: one is that high-temperature annealing removes dopants and thus increases the electrical resistivity of the sample [15,16]; and the other is that high-temperature annealing improves the tube–tube contacts such that carriers can move more freely from one tube to another. But the reduction of dopants may also weaken the tube–tube contacts [16]. The key issue is whether the transport behavior of these bulk samples is dominated by inter-tube coupling or intra-tube effects. For our samples, the electrical conduction is likely through variable-range hopping. As shown in the inset of Fig. 2b, the electrical resistivity shows linear behavior when plotted as \( \log[\rho/\rho(300\,\text{K})] \) versus \( T^{-1/4} \) below ~20 K for all samples. Such relation describes systems with three-dimensional (3D) character in electrical conduction [17]. If it were dominated by intra-tube conduction, the 1D character with \( \log[\rho/\rho(300\,\text{K})] \propto T^{-1/2} \) is expected. Thus, it is conceivable to state that the low-temperature electrical conduction is dominated by tube–tube contacts for our samples. The enhanced upturn of the electrical resistivity observed in annealed samples suggests that the tube–tube

![Fig. 1. (color online) (a) A demonstration showing a sample (left) detached from the vertically aligned arrays of CNTs (right); (b) a sample with four contacts, where the geometric factors (cross-section area \( A \) and the length \( L \) between two inner contacts) are indicated; (c) and (d) are HRTEM images of CNTs for samples S1 and S4, respectively.](image-url)
contacts become worse upon annealing. As will be discussed below, it is likely that our as-grown sample contains oxygen that is adsorbed on the surface of CNTs [7,8]. Annealing in Ar atmosphere may reduce the adsorbed oxygen content [9,10], thus weakening tube–tube contacts and changing the carrier concentration as confirmed by TEP and thermal conductivity data.

Shown in Fig. 3a is the temperature dependence of TEP $S$ for samples S1–S4. Similar to that observed in single-wall CNTs [6,9–13], $S$, for all samples, varies roughly linearly with $T$ over a wide temperature range, as expected for metallic CNTs [9,18]. For sample S4, $S$ clearly deviates from high-temperature behavior below $T_x \sim 50$ K, where the thermal conductivity shows the dimensional crossover (see below). Similar to that observed in single-wall CNTs (sample b in Ref. [19]), the magnitude of the derivative of the TEP for S4 increases with increasing $T$ below $T_x$ (see Fig. 3b). This suggests that the TEP of S4 is controlled by the phonon drag at low temperatures, as discussed previously [19,20]. Strikingly, $S$ decreases with increasing annealing temperature and changes sign from positive (S1, S2, S3) to negative (S4). This indicates that the sample annealed at 2800°C changes the dominant carrier type from hole like to electron like. Theoretically, the TEP of CNTs is expected to be small due to its mirror symmetry of band structure [18,21]. It has been argued that the large and positive TEP of CNTs is due to the presence of oxygen. According to Refs. [7,8], the existence of oxygen causes metallic behavior in semiconducting nanotubes and the positive sign of TEP is caused by the partial transfer of electrons from the nanotubes to oxygen molecules adsorbed on the CNTs. Measuring TEP in vacuum or inert gas (N$_2$, He or Ar) environment results in a negative value for single-wall CNTs [8–10,12]. Our data shown in Fig. 3a

![Fig. 2. (a) Temperature dependence of the electrical resistivity for samples S1–S4. Displayed in (b) is the replot of the data by normalization to 300 K. Inset is log(ρ/ρ(300 K)) versus $T^{-1/4}$.](image)

![Fig. 3. (a) Temperature dependence of thermoelectric power for S1 (empty circles), S2 (solid circles), S3 (crosses) and S4 (solid diamonds). Note TEP for S4 is negative; (b) plot of the derivative d$S$/dT versus $T$ for S4; (c) variation of the TEP at room temperature with annealing temperature. The expected threshold annealing temperature range for sign reversal of $S$ is marked with shadow.](image)
reveal exactly the same tendency, possibly resulting from the same origin: if the as-grown sample S1 contains adsorbed oxygen, it may be reduced or completely removed via annealing in Ar atmosphere, leading to sign change of TEP from positive to negative. Our results suggest that higher an annealing temperature is more effective for the removal of the adsorbed oxygen. To estimate the threshold higher an annealing temperature is more effective for the TEP from positive to negative. Our results suggest that via annealing in Ar atmosphere, leading to sign change of adsorbed oxygen, it may be reduced or completely removed the same origin: if the as-grown sample S1 contains physically adsorbed oxygen in our CNT samples, it is known that the chemisorbed oxygen requires high temperatures to be removed [22], and is often located at defects sites or on the open ends of the nanotubes [23]. Our results demonstrate that higher an annealing temperature is more effective for chemisorbed oxygen removal. As will be discussed below, the removal of chemisorbed oxygen also improves the crystallinity of the nanotubes, thus enhancing the thermal conductivity.

Is oxygen the sole source that alters the sign of TEP of CNTs? Previous work indicates that the presence of transition metals M from the catalyst may strongly affect the TEP via interaction between the magnetic moment of the M and the spins of the conduction π electrons of the nanotubes, i.e. the Kondo effect [7]. This results in anomalously large and positive TEP with a peak-like feature and a upturn of the electrical resistivity at low temperatures. The TEP for all of our samples varies rather smoothly with temperature. This suggests that the contribution from Fe particles (if there are some) is unimportant in our samples, although the as-grown sample was prepared using Fe as a catalyst. On the other hand, the high-temperature annealing removes and/or carbonizes the catalytic particles according to Refs. [14,23]. Thus, sample S4 may contain the least amount of catalytic particles among all four samples and its negative TEP may reflect the intrinsic character of CNTs, similar to the highly oriented pyrolytic graphite [20].

As mentioned above, the removal of catalytic particles or dopants may weaken the tube–tube contacts, if they were at the surface of the CNTs. In this case, the thermal conductivity may be reduced as observed previously [14,24]. Displayed in Fig. 4 are the thermal conductivity κ data for samples S1–S4. Similar to previous observations [15,16,25–27], κ increases with increasing T for all samples, showing no sign of turnover (negative dκ/dT) like that seen in individual MWCNT [4] and in graphite and diamond [28]. While it is roughly two orders of magnitude smaller than that obtained from an individual MWCNT [4], κ increases with increasing annealing temperature except for S3. This may again be due to the error in estimating the geometric factors (see Fig. 1b). Since the geometric factors involved in measuring κ and ρ are identical, the fraction of the heat carried by electrons may be estimated by the Wiedemann–Franz law, i.e. $κ_e = L_0 T/ρ$ with $L_0 = 2.45 \times 10^{-8} (\text{V/K})^2$. This yields the maximum $κ_e \sim 0.04 \text{W/K} \text{m}$ at 300 K, much smaller than the measured κ value. It is thus clear that the thermal conductivity is dominated by phonons throughout the entire temperature range. The continuous increase of κ with increasing T suggests high Debye temperature for MWCNTs, consistent with specific heat measurements [24].

In view of Fig. 4, it may be seen that, in addition to the magnitude difference ($κ(S4)/κ(S1)\sim 9$ at 300 K), $κ(T)$ for S4 has convex shape, while the rest show a concave feature. We note that the convex-shaped $κ(T)$ is observed for samples consisting of either individual CNT [4] or aligned CNTs [16,27], while concave-shaped $κ(T)$ is seen in systems with heat flow perpendicular to CNTs [27]. This suggests that high temperature annealing improves crystallinity, as confirmed by TEM images (see Figs. 1c and d). Thus, phonon scattering from the tube–tube junctions may be considerably reduced in S4 [4]. The particular temperature dependence of $κ(S4)$ also reflects the low-dimensional heat transport character. As may be seen in the inset of Fig. 4, $κ(T)$ for S4 exhibits linear behavior above $T_x\sim 50 \text{K}$ when
plotted in double logarithmic scales. This indicates that $\kappa(T)$ for S4 follows a power law, i.e., $\kappa \propto T^n$. By fitting data between 50 and 300 K, we obtain $n = 0.8$ as indicated by the solid line. Below 50 K, $\kappa$(S4) decreases much faster than that at higher temperatures, thus indicating larger $n$. As the larger $n$ corresponds to higher dimensionality in phonon heat conduction [4,25], the change of $n$ value in S4 suggests a crossover of dimensionality from low-dimensional character at high temperatures to high-dimensional heat conduction at low temperatures. The characteristic temperature $T_x$ is similar to that observed in TEP (see Fig. 3) and in MWCNTs [4]. For comparison, we also extracted the exponent for the as-grown sample S1, where $\kappa$ follows $T^{-1.35}$ and shows no sign of dimensional crossover in the entire temperature range (see the inset of Fig. 4). The absence of dimensionality crossover suggests that the highly resistive thermal junctions between the tubes largely dominate the thermal transport in S1.

Overall, both electrical and thermal transport properties of macroscopic bundles of long MWCNTs are clearly altered by high-temperature annealing. With increasing annealing temperature, both electrical resistivity and thermal conductivity tend to increase, but the TEP decreases and changes sign from positive to negative. These can be attributed to the improvement of crystallinity of the nanotubes and the reduction of chemisorbed oxygen through annealing. Our systematic study demonstrates that higher an annealing temperature is more effective for the purpose of improving the quality of CNTs.

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