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Thermal conductivity of high performance carbon nanotube yarn-like fibers

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In the present paper, we present results of thermal conductivity measurements in free standing carbon nanotube (CNT) yarn-like fibers. The measurements are made using a T-type experimental configuration utilizing a Wollaston-wire hot probe inside a scanning electron microscope. In this technique, a suspended platinum wire is used both as a heater and a thermal sensor. A low frequency alternating current source is used to heat the probe wire while the third harmonic voltage across the wire is measured by a lock-in amplifier. The conductivity is deduced from an analytical model that relates the drop in the spatially averaged temperature of the wire to that of the sample. The average thermal conductivity of the neat CNT fibers and the CNT –polymer composite fibers is found to be 448 W/m-K and 225 W/m-K, respectively. These values for conductivity are amongst the highest measured for CNT yarn-like fibers fabricated using a dry spinning process from vertically aligned CNT arrays. The enhancement in thermal conductivity is understood to be due to an increase in the CNT fiber elastic stiffness during the draw and twist operations, lower CNT thermal contact resistance due to increase in CNT contact area, and better alignment of the CNT fibrils along the length of the fiber. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4874737]

I. INTRODUCTION

In recent years, nanotube assemblies in high-packing density and aligned configurations have been developed, which offer a promising route to achieve higher strength and transport properties in macroscopic materials. While the primary focus has been on production of these materials and on their mechanical and electrical properties,1–9 other properties including thermal conductivity are of both fundamental interest and importance for applications such as heat dissipation in composite structures and thermal interface materials. With a focus on experimental results, this paper addresses thermal conductivity in carbon nanotube (CNT) yarn-like fibers.

In the recent past, two distinct synthesis routes have been utilized in the fabrication of neat CNT yarn-like fibers10 – the first route employs a solid-state process wherein CNTs are either directly spun into a fiber from the synthesis reaction zone11 or from a CNT forest array grown on a solid substrate.9 The approach, however, does not lend itself to easy scale up since it combines multiple steps, limiting options for process and material optimization. Fibers fabricated using this approach have been shown to have low packing density and poor orientation and include impurities within their structure.12 Despite these shortcomings, solid-state CNT fibers have delivered the best mechanical properties thus far.1,11,13,14 The reason for this success is understood to be the length of CNTs that constitute these fibers.10 Longer CNTs reduce the number of CNT ends (junctions) in a typical fiber, yielding greater strength,15 and may also increase electrical and thermal conductivity.16 The alternate fiber production route is wet spinning.1 In this process, the CNTs are dissolved or dispersed in a fluid, extruded out of a spinneret, and then coagulated into a solid fiber by extracting the dispersant. The process can easily be scaled to industrial levels and is the route by which traditional high performance fibers, such as Kevlar, are manufactured.17 Decoupling synthesis of CNTs from spinning of the fibers also allows independent optimization of the two steps and enables CNT purification. Recently, using this approach, Behabtu et al.18 have shown that exciting properties can be achieved by wet-spinning CNTs into high-performance, multifunctional fibers.

As mentioned earlier, even though numerous studies have been conducted to characterize mechanical and electrical properties of the CNT yarn-like fibers, only a few thermal conductivity measurements have been made to date. Ericson et al.19 reported a measured thermal conductivity of 21 W/m-K for a CNT fiber manufactured using a wet-spinning process. Aliev et al.13 measured thermal conductivity and thermal diffusivity of a CNT web to be 50 W/m-K and 45 mm2/s, respectively, in a direction parallel to the web and 26 W/m-K and 62 mm2/s for the yarn. These relatively low thermal conductivity values were attributed to the non-homogeneity of the fiber web structure, existence of nanotube defects, and the extremely high surface area that was responsible for excessive radial heat radiation. In an another study, thermal conductivity of 26 W/(m·K) was reported for yarn drawn from a 300 μm tall CNT array,19 which was only slightly higher than the 20 W/(m·K) reported for single wall CNT fibers extruded from the super-acid suspension of much shorter CNT.20 Recently, Jakubinek et al.21 synthesized CNT yarns of diameter ca. 15 nm by spinning from vertically aligned CNT arrays approximately 500 μm tall. The spun yarns had a density of about 0.9 g/cc and a twist angle of about 1 × 104/m, and showed much improved electrical and thermal conductivities due in part to their higher density.22 For example, for a multi-wall carbon
nanotubes (MWCNT) yarn of 10 μm diameter the room temperature thermal conductivity was measured to be ca. 60 ± 20 W/(m·K), which was the highest reported for a CNT yarn to date.

More recently, Behabtu et al.18 have fabricated solid CNT fibers by utilizing a high-throughput wet spinning process, the same as that used to produce high-performance industrial fibers. To understand the relative importance of CNT alignment, packing density, and doping on the mechanisms of electrical and thermal conduction in these fibers, they studied the temperature-dependent conductivity of annealed CNT fibers and isotropic films as well as acid-doped and iodine-doped CNT fibers. They reported an average thermal conductivity of 380 ± 15 W/(m·K) in ca. 1.5-mm-long CNT fiber samples. Iodine doping was observed to double the thermal conductivity to 635 W/m·K. These reported thermal conductivity values are about 20% of individual CNT values, possibly due to quenching of the phonon modes by the inter-CNT coupling, but 10 to 100 times that of other macroscopic CNT samples usually limited by weak inter-CNT transport due to misalignment.

In the present study, we focus on thermal conductivity measurements in CNT yarn-like fibers fabricated by using a solid-state sequential “draw and twist” of CNT strips out of vertically aligned CNT forests.21,23 Besides thermal conductivity measurements in CNT fibers, we also characterize thermal conductivity in higher strength CNT yarn-like composite fibers fabricated by infiltration of PVA resin into the neat CNT fibers. The resulting volume fraction of PVA in the CNT fibers is ~20%. In order to make the thermal conductivity measurements in the CNT fibers, we utilize the 3ω Wollaston wire T-type probe method.24,25 In this technique, a suspended wire of known electrical resistivity and temperature coefficient of resistance is Joule heated by a current source until it reaches steady-state. After attaching the CNT fiber to the hot wire probe, the sample thermal conductivity is determined from the average temperature drop and the sample geometry. The method has been successfully used by the authors in the past to obtain the thermal properties of carbon nanofibers and CNT.25,26

II. EXPERIMENTAL METHODS

A. Carbon nanotube fiber samples

The samples studied in this work were fabricated using a dry-spinning process comprising sequential pulling and twisting of individual CNTs from a vertically aligned CNT forest by Prof. Qingwen Li and co-workers at the Suzhou Institute of NanoTech and Nano Bionics, China. The fiber specimens were provided for thermal characterization to Case Western Reserve University (CWRU) by Prof. Tsu-Wei Chou of the University of Delaware.

A schematic of the CNT fiber spinning is shown in Figure 1. The vertically aligned CNT arrays were grown at atmospheric pressure on SiO2/Si wafers. The wafer was coated directly with a thin Fe film by electron beam evaporation and C2H2 gas was used as the carbon source. The substrate was then placed inside a semi-opened boat and heated in flowing Ar gas to a growth temperature of 660–750 °C for 5–10 min. The resulting multi-wall carbon nanotubes had a diameter of 8–10 nm with ≤6 walls. The array height was ~320 μm and Raman spectroscopy confirmed an IG/ID ratio of ~0.99. The mechanical strength and modulus of the individual tubes were determined21 to be 866 MPa and 16 GPa, respectively. The higher strength CNT yarn-like composite fibers were fabricated by infiltration of Polyvinyl alcohol (PVA) resin into the neat CNT fibers. The resulting volume fraction of PVA in the CNT fibers was ~20%. Because of the strong interfacial bonding between CNT and PVA,27 these composite fibers have been shown to possess considerably improved mechanical properties.21

Figures 2 and 3 show high magnification SEM images of the CNT fiber and CNT-polymer composite fibers, respectively. The images of the CNT fibers show clear evidence that the fibers are derived from CNTs and are twisted during the manufacturing process. Further details of the fiber fabrication process and their mechanical properties can be found in the several research articles.28–34

Raman spectroscopy is used to examine the degree of graphitization and the composition of the CNT fibers and the CNT-polymer composite fibers. The excitation wavelength employed for this assessment is 785 nm. The analysis of the sample quality is made by observing the ratio of the D band peak intensity (occurring at ~1308 cm−1) and the G-band peak intensity (occurring at ~1580 cm−1) as shown in Figure 4. The D-band peak intensity is due to the disordered graphite material, and the G-band peak intensity is due to the ordered graphite material. The ratio of D/G peak intensity gives an indication of the graphitization degree of the CNT fibers.

FIG. 1. Schematic of the dry-spinning of CNT fibers by pulling CNTs from a vertically aligned CNT array.

FIG. 2. SEM micrographs of the CNT fiber at nominal magnifications of (A) 4000×, (B) 20000×, (C) 50000×, and (D) 100000×.
peak intensity (occurring at \( \sim 1596 \text{ cm}^{-1} \)). The D band is associated with the loss of symmetry of atoms at the graphene sheet boundaries, which appears in the form of defects and carbonaceous impurities. The G band is associated with \( \text{sp}^2 \) bonding in the carbon systems, and it indicates the amount of graphitization in the sample. A lower D/G ratio of band intensity indicates that the sample batch has fewer defects and a higher degree of graphitic crystallinity. However, the technique provides only a qualitative comparative study of defects in the neat and polymer-reinforced CNT composite fibers.

Figures 4(a) and 4(b) compare the Raman intensities in CNT fiber and the CNT-polymer composite fibers, respectively. The D/G ratios for each sample are nearly identical \(-1.15 \) for the pure CNT fiber and \( 1.16 \) for the CNT-polymer composite fiber. This indicates that the carbon structures of the two fibers are nearly the same, and the primary difference between the two is the presence of the polymer for the CNT composite fiber. The peak labeled as the polymer peak in Figure 6(b) occurs around \( 1190 \text{ cm}^{-1} \). This peak has also been shown to be present in other studies of CNT-polymer composites.\(^{35}\)

**B. Thermal conductivity measurements using a T-type probe**

A T-type probe composed of a Wollaston wire is employed to obtain the thermal characteristics of free standing CNT fiber samples.\(^{24}\) The Wollaston wire has the advantage of being extremely cost effective when compared to conventional microfabrication methods,\(^{36}\) and allows for a large volume of samples to be characterized in a short span of time. To date, the T-type method has also been used to measure thermal conductivity of a variety of microscale samples.\(^{37-40}\) The details regarding the technique, including configuration and analysis for extracting thermal conductivity in one dimensional nanostructures are provided in Bifano et al.,\(^{25}\) and are discussed briefly here.

In view of the relatively long length of the CNT yarn-like fibers, the analysis reported in Bifano et al.,\(^{25}\) has been extended to include radiation heat losses in the CNT fiber samples.

Figure 5 shows a schematic of the T-type hot-wire (henceforth referred to as the probe wire) thermal conductivity measuring system, the physical model, and the coordinate system used in the analysis. The probe wire is supported with lead wires (heat sink at ambient temperature) at each end and supplied with a known low frequency alternating current to generate a uniform heat flux in the hot wire. The CNT fiber sample is attached to the center position of the probe wire at one end while the other end is connected to the manipulator probe tip which also acts as a heat sink. Both ends of the probe wire as well as the end of the sample fiber attached to the heat sink are maintained at the ambient temperature during the experiment.

The temperature at the junction between probe wire and the sample CNT fiber depends on the thermal conductivity of the probe wire and the sample fiber, the heat generation rate in the probe wire, and the heat transfer coefficients (radiation losses) around the probe wire and sample fiber. In this way, if we know exactly the relationship between these quantities through the solution of one-dimensional steady-state heat conduction along the probe wire and the sample fiber we can obtain the thermal conductivity of the sample fiber by measuring the heat...
generation rate and the corresponding average temperature change in the probe wire.

1. Basic equations and boundary conditions

As described above, both ends of the probe wire and one end of the sample fiber are supported with the lead wires that have a high thermal conductivity and a large heat capacity compared to those of the probe wire and the sample fiber. Therefore, the temperature at the two ends of the probe wire and one end of the sample fiber can be assumed to maintain the initial (ambient) temperature during the experiment. Assuming a uniform temperature in the radial direction for both the probe wire and the sample fiber due to their small Biot number \((Bi = \frac{hD}{2k})\), where \(h\) is the heat transfer coefficient, \(D\) is the diameter, and \(k\) is the thermal conductivity of the probe wire or the sample fiber), the steady state thermal response of the probe wire and the sample fiber can be modeled using relevant one-dimensional heat conduction equations as follows:

For \(-L_p/2 < x < 0\) and \(y = 0\)

\[
d^2\theta(x) = -\frac{Q_{RMS}}{k_P A_p L_p}.
\]

(1)

For \(0 < x < L_p/2\) and \(y = 0\)

\[
d^2\theta(x) = -\frac{Q_{RMS}}{k_P A_p L_p}.
\]

(2)

For \(x = 0\) and \(0 < y < L_F/2\)

\[
d^2\frac{\theta_F(y)}{dy^2} - m^2 \theta_F = 0; \quad \text{where} \quad m^2 = \frac{4h_F}{k_F D_F} \quad \text{and} \quad h_F \approx 4e_F \sigma \theta_0^4.
\]

(3)

In Eqs. (1)–(3), \(\theta(x)\) is the spatial temperature rise in the probe wire with \(\theta^-(x)\) and \(\theta^+(x)\) representing the temperature distributions in the probe wire in the range \(-L_p/2 < x < 0\) and \(0 < x < L_p/2\), respectively; \(\theta_F(y)\) represents the temperature distribution in the sample fiber along the \(y\)-axis; \(Q_{RMS}\) is root mean square heat generated due to Joule heating of the probe wire; \(k_P, A_P, L_P\) are the thermal conductivity, cross-sectional area, and the length of the probe wire, respectively; \(k_F, D_F, h_F\) are the thermal conductivity, diameter, and the heat transfer coefficient of the sample fiber, respectively; \(\theta_0\) is the average of the ambient and the sample fiber temperatures and is taken to be \(\theta_0 \approx 298\) K; \(e_F\) is the emissivity of the sample fiber and is taken to be unity corresponding to a perfect black body; and \(\sigma = 5.670373 \times 10^{-8}\) W m\(^{-2}\) K\(^{-4}\) is the Stefan-Boltzman constant.

In our present analysis, heat loss due to convection and radiation in the hot-wire probe is assumed to be negligible since all the thermal characterization experiments are conducted in vacuum inside a high resolution SEM and are made using very small heating amplitudes and with probe wires with relatively small lengths. However, because of the relatively long length of the sample fibers, the radiation heat loss from the fiber is expected to be significant, and is thus included in the thermal analysis of the sample fiber (Eq. (3)).

Equations (1)–(3), are solved along with the following boundary conditions:

At \(x = 0\) and \(y = 0\)

\[
\theta^-(x = 0) = \theta^+(x = 0) = \theta_F(y = 0),
\]

(4)

and

\[
q_1(x = 0, y = 0) + q_2(x = 0, y = 0) = q_3(x = 0, y = 0),
\]

(5)

where
In this way, the thermal characteristics of the sample fiber are incorporated into the model by a flux boundary condition at the point of sample attachment \((x=0, y=0)\), to the probe wire.

At \(x = \pm L_p/2\) and \(y=0\)
\[
\theta^0(\pm L_p/2, y=0) = 0 \quad \text{and} \quad \theta^{+}(L_p/2, y=0) = 0.
\]  

At \(x = 0\) and \(y = L_p\)
\[
\theta_F(x=0, y=L_p) = 0. \quad (7)
\]

The piecewise parabolic solution for the temperature distribution in the probe wire can be expressed as
\[
\theta(x, \eta') = \frac{Q_{RMS}L_p}{8k_pA_p} \left[ \left(1 - \frac{x}{L_p/2} \right)^2 + \left( \frac{\eta'}{1+\eta'} \right) \right] \times \left( \frac{x}{L_p/2} - 1 \right), \quad (8)
\]

where the parameter \(\eta'\) is the ratio of the thermal resistance of the probe wire \(R_{th,F}\) to the apparent thermal resistance of the sample fiber \(R'_{th,F}\), and is defined as \(\eta' = R_{th,F}/4R'_{th,F}\). The thermal resistance of the probe wire and the apparent thermal resistance of the sample are given by \(R_{th,F} = L_p/k_pA_p\) and \(R'_{th,F} = R_{th,c1} + R_{th,c2} \tanh(mL_p)/(mL_p) + R_{th,c2}\), respectively, where \(R_{th,c1}\) is the thermal contact resistance at the probe wire and sample CNT fiber junction, \(R_{th,c2}\) is the thermal contact resistance at the sample fiber and the manipulator tip (heat sink) junction, and \(R_{th,F} = L_p/k_pA_p\), is the true thermal resistance of the sample fiber under investigation. Note that if we neglect the radiation heat loss in the sample fiber (i.e., \(m \to 0\)), \(R'_{th,F} = R_{th,c1} + R_{th,F} + R_{th,c2}\). Also, in the absence of the sample, i.e., \(R'_{th,F} = \infty\), \(\eta = 0\), and the well-known inverted parabolic temperature solution for a Joule heated suspended wire is recovered.

In our present work, the apparent thermal resistance of the fiber sample can be simplified to \(R'_{th,F} \approx R_{th,F} \tanh(mL_p)/(mL_p)\), since both \(R_{th,c1}\) and \(R_{th,c2}\) are expected to be negligibly small, as shown in a previous study on CNT by the authors. In that work, at 293 K, CNT and heat sink junctions created with Pt electron beam induced deposition (EBID) and the amorphous carbon EBID were determined to have thermal contact resistance of \(5.79 \times 10^{-9}\) Km²/W and \(5.18 \times 10^{-9}\) Km²/W, which are consistent with theoretical estimates and experimental data for interfaces. The reduction in contact resistance that occurs when using EBID results from the increased contact area at the sample fiber-probe junction and the sample fiber-manipulator tip. One of the challenges in using EBID with the CNT yarn-like fibers is the relatively large diameter of the fibers (~12 μm to 15 μm) when compared to the diameter of individual CNTs (10 nm to 50 nm) used by the authors in Bifano et al. The larger diameter makes it practically very difficult, due to the slow deposition rate of EBID, to build up the required thickness (i.e., larger than the diameter of the fibers) of carbon/platinum deposition so as to reliably clamp the relatively large diameter CNT fibers to the substrate. Consequently, in the present study, silver epoxy was used instead of carbon/platinum EBID for bonding the CNT fiber samples to substrate. Because of the higher thermal conductivity of the silver epoxy when compared to platinum/amorphous carbon deposits, with the use of the silver epoxy the thermal contact resistance is expected to be smaller when compared to sample CNT fiber junctions formed by using EBID. The presence of additional mass of epoxy at these interfaces is not expected to affect the steady state temperature profile as long as the diameter of the platinum probe wire is not altered to interfere with the 1D thermal transport assumption. For similar reasons, the use of silver epoxy at the junctions is likely to help enforce the constant temperature boundary conditions at the manipulator-sample attachment point.

Integrating Eq. (8) over the length of the probe wire, the spatially averaged temperature rise \(\bar{\theta}\) over the length of the sample can be written as
\[
\bar{\theta} = \frac{1}{12} Q_{RMS} R_{th,F} \left(1 - 3\frac{(\eta')^2}{4(1+\eta')}\right). \quad (9)
\]

2. Experimental procedure

In order to conduct the three omega measurements, the platinum probe wire is heated using a low-frequency current, \(I(t) = I_{1o} \cos \omega t = I_{1o} \cos \omega t \sqrt{2} \cos \omega t\), where \(I_{1o}\) is the current amplitude and \(I_{1o}RMS\) is the RMS current. The current used to Joule heat the Pt probe is driven at a sufficiently low frequency to prevent a phase shift in the heating frequency and the temperature rise. This is achieved by choosing a heating frequency whose period is much greater than the thermal diffusion time \(\tau = L_p^2/k_p\alpha\) of a suspended wire.

For sufficiently low heating currents \(I(t)\), the Joule heating in the wire is given by
\[
Q(t) = I^2(t)R_{eo} = I^2_{1o}RMSR_{eo} \cos \omega t + 1/2, \quad (10)
\]

where \(R_{eo}\) is the electrical resistance of the probe wire at zero current. For low frequency current and under quasi-steady state, the spatially averaged temperature of the probe wire, \(\bar{\theta}(t)\), can be taken to be directly proportional to Joule heating by the thermal transfer function \(Z_o\) such that \(\bar{\theta}(t) = Z_o Q(t)\).

When the wire is Joule heated, the third harmonic voltage across the wire is given by
\[
V_{3o,RMS} = \frac{1}{2} Z_o I_{1o} RMS Q_{RMS} R_{eo}, \quad (11)
\]

where \(Q_{RMS} \equiv I^2_{1o}RMSR_{eo}\) is the RMS Joule heating. Defining the third harmonic RMS electrical resistance as
The ratio of the slopes is then defined as

\[ R_{\text{cross-sections}} = \frac{V_{3\omega,\text{RMS}}}{I_{\omega,\text{RMS}}} \]

Using Eq. (12), the thermal transfer function \( Z_o \) can be experimentally determined by obtaining the slope of the \( R_{3\omega,\text{RMS}} \) versus \( Q_{\text{RMS}} \) plot.

In view of Eqs. (9) and (12) the theoretical thermal transfer function can be written as

\[ Z_o = \frac{1}{12} R_{3\omega,\text{P}} \left( 1 - \frac{3}{4} \left( \frac{\eta'}{1 + \eta'} \right) \right) \]

When no sample is attached, \( \eta' = 0 \); using Eq. (12), the thermal resistance of the probe wire is deduced to be

\[ R_{3\omega,\text{P}} = \frac{24}{2R_{\omega,\text{co}}} \left( \frac{\Delta R_{3\omega,\text{RMS}}}{\Delta Q_{\text{RMS}}} \right) \]

The ratio of the slopes is then defined as

\[ \phi = \frac{(\Delta R_{3\omega,\text{RMS}}/\Delta Q_{\text{RMS}})_{\text{With Sample}}}{(\Delta R_{3\omega,\text{RMS}}/\Delta Q_{\text{RMS}})_{\text{No Sample}}} \]

and the apparent sample thermal resistance can be found via Eqs. (14) and (15), to be

\[ R'_{3\omega,\text{F}} = \frac{1}{4} R_{3\omega,\text{P}} \left( \frac{1}{4(1 - \phi)} - 1 \right) \]

The thermal conductivity of the sample can then be determined by iteratively solving for \( k_F \) from \( R'_{3\omega,\text{F}} \approx R_{3\omega,\text{F}} \tanh(mL_F)/(mL_F) \). Note: in the calculation of thermal conductivity the samples are taken to have solid cross-sections.

3. Heater/sensor for three omega CNT fiber and CNT-polymer composite fiber experiments

The probe wires used for the measurement of the sample CNT fibers and CNT-polymer composite fibers are constructed from commercially available Wollaston wire obtained from the Goodfellow Corporation. The wires are composed of a 99.9% platinum core with a nominal diameter of 5 \( \mu \)m, surrounded by a silver sheath approximately 40 \( \mu \)m in diameter. A total of two Wollaston wire probes can be mounted on the device as shown in Figure 6. The probes are soldered to copper pads using low temperature solder (Cerroloy-117 alloy). Each probe wire is etched using 10% aqueous nitric acid such that a nominal length of 4 mm of the platinum core is exposed.

An important consideration in the design of the test apparatus is ensuring that the thermal resistance of the probe wire is properly matched to the thermal resistance of the sample.25 Thermal resistance matching ensures that the sensitivity of the temperature response of the probe wire to the sample is high so that small changes in sample thermal resistance result in relatively large changes in the spatially averaged temperature rise in the probe wire. Following Bifano et al.,25 it can be shown that \( \eta' \) must be between 0.077 and 12.923 to keep the uncertainty in measured sample resistance within ten percent of the true value.

The heating/sensing device used in the thermal conductivity measurements of the CNT fibers and CNT-polymer composite fibers is first verified by measuring thermal conductivity in 99.9% purity Au wire with a nominal diameter of 20 \( \mu \)m; the Au wire is chosen as a benchmark sample because of its uniformity in diameter. The 3\( \omega \) thermal conductivity measurements yielded measurements of 312 \( \pm \) 7 \( \text{W/m-K} \) and 290 \( \pm \) 7 \( \text{W/m-K} \) in the Au wire. These values are 2.0% and 8.8% less than the literature value of 318 \( \text{W/m-K} \) for 99.99% purity Au wire. Thus, the experimental setup and methods employed for characterizing thermal conductivity in CNT fiber and CNT-polymer composite fiber were considered to be valid.

III. RESULTS AND DISCUSSION

A. Thermal conductivity of CNT fibers and CNT-polymer composite fibers

Thermal conductivity measurements were made in both the neat CNT fibers as well as the CNT-polymer composite fibers. Images of an example experiment conducted on a CNT-polymer composite fiber are shown in Figure 7.

The length, diameter, and the measured apparent and true (radiation heat loss corrected) thermal conductivities for

![FIG. 7. Image (A) of experimental setup with CNT-polymer composite sample attached. The platinum core of the Wollaston wire is labeled (a). The CNT-polymer composite fiber, labeled (b), is attached to the probe wire and low-temperature solder (ambient temperature heat sink) by thermally conductive silver epoxy. The low-temperature solder with thermally conductive silver epoxy is labeled (c). The setup with the shown sample is representative of all experiments conducted on the CNT fibers and CNT-polymer composite fibers. Images (B) and (C) show the sample-probe wire contact and sample-heat sink contacts in greater detail.](image-url)
the CNT fiber samples and CNT-polymer composite fiber samples are listed in Table I and Table II, respectively. The standard deviation associated with length is due to the uncertainty in measurement of the length, while the standard deviations associated with the diameter are dominated by diameter variation along the length of the sample rather than uncertainty in the measurement of the diameter. Thus, measurements made on samples with significant diameter variation along the length of the sample result in large error bars for the thermal conductivity.

Figure 8 shows the thermal conductivity for the two sets of samples. The average true thermal conductivity for the CNT fibers was 448 ± 61 W/m-K and 225 ± 15 W/m-K for the CNT-polymer composite fibers. The standard deviation associated with the average value reflects the variation in individual sample thermal conductivity measurements rather than uncertainty in the measurements themselves.

The measurements reported in this study are by far the highest measured thermal conductivities reported for CNT fibers.10,13,18,21,44,45 fabricated using solid state draw and twist processing of CNT films directly from vertically aligned multi walled carbon nanotube arrays. The previous maximum thermal conductivity was reported by Jakubinék et al.21 to be 60 W/m-K. While the mechanism for thermal transport in CNT fibers is not well understood,30 there are a few noteworthy factors that are understood to contribute to the much larger thermal conductivity.

Before discussing the aforementioned results on CNT fibers, it is instructive to look at results of thermal conductivity measurements obtained on aligned CNT bundles. In general, experimental results have shown the thermal conductivity of CNT bundles to be lower than those obtained for individual CNTs,25,46,47 even when the low apparent density of bundles is taken into account. Simulations indicate that thermal conductivity decreases by roughly a factor of three for close-packed bundles in comparison to individual SWCNTs.48

TABLE II. CNT-polymer composite fiber sample dimensions and the measured apparent and true (radiation heat loss corrected) thermal conductivities.

<table>
<thead>
<tr>
<th>Length (mm)</th>
<th>Diameter (μm)</th>
<th>Apparent thermal conductivity of CNT fibers (W/m-K)</th>
<th>True thermal conductivity of CNT fibers (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00 ± 0.01</td>
<td>14.6 ± 0.5</td>
<td>322 ± 22</td>
<td>287 ± 12</td>
</tr>
<tr>
<td>8.34 ± 0.06</td>
<td>14.1 ± 1.0</td>
<td>358 ± 52</td>
<td>256 ± 25</td>
</tr>
<tr>
<td>9.42 ± 0.02</td>
<td>12.8 ± 0.5</td>
<td>216 ± 16</td>
<td>131 ± 10</td>
</tr>
</tbody>
</table>

The effect of bundle size was explored by Aliiev et al.,44 who measured thermal conductivity in individual CNTs and CNT bundles of increasing size and found that the thermal conductivity decreased by approximately four times as the bundle size increased to 100 CNTs. The decrease in thermal conductivity in CNT bundles is understood to be attributed to coupling between CNTs in bundles, where bundles restrict out-of-plane phonon vibrations and therefore suppress low lying optical modes that are known to contribute significantly to thermal conductivity at room temperatures. When heat transfer between CNTs is involved, the interface thermal resistance between the nanotubes further reduces thermal conduction. In this case, heat transfer is inhibited by small contact area and high thermal interfacial resistance at the CNT-CNT contacts, estimated from simulations to be >10⁻⁸ m²-K/W even for short CNT-CNT separations.59 Such resistances can lead to CNT assemblies with thermal insulating properties. For packed beds composed of 10–20 vol. % CNT produced by compressing random mats of CNT, thermal conductivity <0.02 W/m-K has been reported due to the dominant effect of CNT-CNT thermal contact resistance.50

In the case of CNT fibers, however, the CNT bundles are drawn and twisted from a CNT array. The drawing is expected to improve the fiber alignment along its length while twisting has been shown to decrease the CNT fiber diameter as well as increase its mechanical stiffness. This decrease in the CNT fiber diameter during twisting can be attributed to the collapse of the CNTs in the radial direction due to increased radial compressive stresses and consequently enhanced inter-CNT interactions. The decrease in overall CNT fiber diameter is also expected to reduce the inter-tube spacing between the CNTs. Zhong et al.,46 using molecular dynamics have shown that the decrease in spacing between the CNTs results in a decrease in the interfacial boundary resistance thus increasing the thermal conductivity of the CNT fiber. Moreover, Badaire et al.,24 have shown that alignment of SWCNT within an SWCNT-polyvinyl alcohol composite fiber play a major role in the fiber’s
overall thermal conductivity. In their case, the alignment of the SWCNT in the SWCNT fibers was achieved by axial stretching, and the room temperature thermal conductivity was observed to improve from 4 W/m-K for 21.5% stretch to 10 W/m-K for a 58.4% stretch.

IV. SUMMARY

In the present paper, we present results of thermal conductivity measurements in free standing carbon nanotube strands, CNT yarn-like fibers, and CNT yarn-like polymer composite fibers. Thermal conductivity measurements were made using a T-type experimental configuration utilizing a Wollaston wire hot-probe inside a SEM. In this technique, a suspended platinum wire is used both as a heater and a thermal sensor. A CNT fiber specimens are attached to the midpoint of the suspended platinum wire using conductive silver epoxy, reducing the thermal contact resistance at the sample-platinum wire junction. During the experiment, the platinum wire is heated using a low frequency alternating current source while the third harmonic voltage across the suspended wire is measured by a lock-in amplifier. The thermal conductivity is deduced from an analytical model that relates the source while the third harmonic voltage across the suspended wire is heated using a low frequency alternating current platinum wire junction. During the experiment, the platinum wire is measured by a lock-in amplifier. The thermal conductivity is deduced from an analytical model that relates the

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39Using an analytic 1D steady state model to represent a 1 mm Pt probe wire having a 750 nm diameter, omission of a radiation term in Eq. (7) is found
to contribute approximately 0.5% error in the measured electrical resistance of the probe wire.