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Effects of heat treatment and contact resistance on the thermal conductivity of individual multiwalled carbon nanotubes using a Wollaston wire thermal probe

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Thermal conductivity measurements in commercially available, chemical vapor deposition–grown, heat-treated and non-heat-treated multiwalled carbon nanotubes (MWCNTs) are reported. The thermal conductivity of individual samples is measured using a suspended platinum wire as a thermal resistance probe in a “T-type” configuration. Changes in third harmonic voltage are measured across the heated suspended platinum wire as a specimen is attached to the platinum wire’s midpoint. An analytic model is used to correlate the reduction in the average temperature of the probe wire to the thermal resistance (and thermal conductivity) of the attached sample. Experiments are implemented inside a scanning electron microscope equipped with nanomanipulators for sample selection, and a gas injection system for platinum based electron beam-induced deposition to improve thermal contact resistances. The results indicate a nearly 5-fold increase in the average thermal conductivity of MWCNT samples annealed with a 20-h 3000 °C annealing heat treatment compared to the as-grown samples. However, specimen-specific morphological defects, such as kinking, Y-branches, etc., are found to negate, to a large degree, the advantage of the heat treatment process. The thermal contact resistance between the MWCNT and the electron beam–induced deposition contacts is estimated using an anisotropic diffusive mismatch model that includes the effect of fin resistance. Adjusting the thermal conductivity to include the effect of thermal contact resistance is found to increase the thermal conductivity by approximately 5%. Once adjusted for thermal contact resistance, the average thermal conductivity of the heat-treated MWCNT specimens is 228 W/m-K, with the highest measured thermal conductivity being 765 ± 150 W/m-K. The results highlight the importance of MWCNT quality in thermal management applications. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3691607]

I. INTRODUCTION

There is little agreement among the few reported thermal conductivity measurements1–5 in MWCNTs. This is likely due to the vast structural and chemical variations in samples. Room temperature thermal conductivity measurements in MWCNTs have been reported to be as high as 3000 W/m-K,1 and as low as 17 W/m-K.5 The chemical vapor deposition (CVD) process commonly used in the synthesis of MWCNTs is known to produce a variety of carbon nanotube qualities depending on growth temperature, catalyst, and carbon source gases used.6

A 2001 study7 showed many structural and chemical improvements in CVD-grown MWCNTs with high temperature annealing. Annealing temperatures that exceeded 2250 °C were found to produce X-ray diffraction patterns similar to those of highly graphitic MWCNTs grown by arc-discharge methods. Smaller interlayer wall spacing, indicative of highly graphitic structures, were also possible with higher annealing temperatures up to 3000 °C. Residual Fe, the primary chemical vapor deposition growth catalyst for MWCNTs, was also found to reduce from 7.1% by wt. after CVD growth to less than 0.01%. Major Fe reduction occurred both at the ends and in the core of the MWCNTs once the annealing temperature surpassed the vaporization temperature of Fe (>1800 °C). While heat treatment improved the microstructural quality of the samples, larger defects that created kinks and branching in the tubes were not removed in the heat-treatment process. More continuous crystalline planes and a reduction in residual catalyst particles are expected to increase phonon mean free path (MFP) and thus increase the lattice (phonon) thermal conductivity in MWCNTs.

More recently, Jin et al.8 reported that annealing of macroscopic MWCNT bundles at 2800 °C for 4 h resulted in a 9-fold increase in thermal conductivity at 300 K (~2.5 to 23 W/m-K). However, from these measurements, an improvement in intrinsic thermal conductivity of an individual MWCNT could not be ascertained. To the authors’ knowledge, heat-treatment effects on the thermal conductivity of individual MWCNTs have not been characterized.

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Over the past 50 years, thermal properties of electrically conductive samples and/or their surrounding media have been investigated by measuring the 3rd harmonic voltage signal produced when a sample is Joule heated via an electric alternating current.

Comparing the measured 3rd harmonic voltage across the sample with an analytic model permits the thermal properties of the sample to be determined. The most simplistic steady-state thermal conductivity measurement method is the “self-heating” technique. In general, the self-heating method requires samples to be electrically conductive, transport heat diffusively, and the temperature coefficient of resistance of the sample to be known. The self-heating method was first applied to a bundle of CNTs and subsequently to individual MWCNTs.

An extension of the self-heating technique is the “T-type probe method,” which replaces the sample with a pre-calibrated suspended wire of known electrical resistivity and temperature coefficient of resistance (Fig. 1). In this way, by attaching a free standing specimen to the probe wire and measuring the reduction in average temperature (inferred from the change in voltage) of the probe wire, the thermal resistance and, thus, thermal conductivity of the specimen is determined. To date, the T-type method has been used to measure a variety of microscale samples. In 2005, Fuji et al. extended the method to a micro-fabricated platinum (Pt) probe that used 3ω voltage detection to measure the thermal conductivity of individual MWCNTs.

In this study, a T-type probe composed of Wollaston wire is implemented. The use of commercially available Wollaston wire was first introduced in 2007 in both 1ω and 3ω configurations for thermal conductivity measurements in individual MWCNTs at room temperature. However, only one measurement of 17 W/m-K was reported. Compared to prior literature values, the low value of the thermal conductivity was attributed either to high thermal contact resistance at the probe-sample interface and/or the possibility of ballistic transport in the short length of sample (380 nm) tested.

Many experimental techniques to measure thermal conductivity in individual nanoscale samples currently employ a micro-fabricated sensing device. Use of commercially available Wollaston wire has the advantage of being extremely cost effective when compared to conventional microfabrication methods and allows for a large volume of samples to be characterized in a short span of time. In the present investigation, all thermal property characterization studies are conducted inside a high-resolution scanning electron microscope equipped with nanomanipulators and a gas injection system. Moreover, the choice of materials and package design allows for multiple Wollaston T-type probes to be prepared with varying thermal resistances and, thus, measurement sensitivities.

II. METHODS

A. Low frequency three omega analysis

In order to conduct the three omega measurements, the probe wire is heated by a low frequency alternating current \( I(t) = I_{1ω} \sin(ωt) \), where \( I_{1ω} \) is the current amplitude. The electrical resistance of the probe wire at zero current is \( R_{eo} \). For sufficiently low heating currents \( I(t) \), Joule heating is assumed to have the form

\[
Q(t) = \dot{F}(t)R_{eo} = \frac{1}{2} \dot{I}_{1ω}^2 R_{eo} (1 - \cos(2ωt)).
\]

While conducting the experiments, attention must be paid to maintain the validity of Eq. (1). The temperature rise of the probe wire must be limited to only a few degrees above ambient temperature. If care is not taken, the average heat input would be better modeled using an iterative \( \dot{Q}(t) = \dot{F}(t)\dot{R}(t) \) instead of \( \dot{Q}(t) = \dot{F}(t)R_{eo} \), resulting in a non-linear dependence of Joule heating on the electrical resistance of the probe wire. The non-linearity is carefully monitored through comparison of linear and quadratic regression models.

The spatially averaged temperature response of the wire \( \dot{θ}(t) \) is proportional to the Joule heating by a thermal transfer function \( Z_o \),

\[
\dot{θ}(t) = Z_o Q(t).
\]

As long as the heating current is driven at a sufficiently low frequency, the thermal response of the probe wire remains in phase with the heating current and the thermal transfer function is largely frequency independent (see Appendix I). Since \( Z_o \) is a function of the thermal resistance of the probe or the probe-sample combination, experimental determination of \( Z_o \) allows the sample’s thermal resistance and, thus, thermal conductivity to be determined.

Using Eq. (2) along with the electrical resistance response of the probe wire, \( \dot{R}_e(t) = R_{eo}[1 + x\dot{θ}(t)] \), where \( x \)
is the temperature coefficient of resistance, the electrical resistance of the probe wire \( R_e(t) \) will experience oscillations at \( 2\omega \) given by

\[
R_e(t) = R_{eo} + \frac{1}{2} aZoJ_{1o}^2 R_{eo}^2 - \frac{1}{2} aZoJ_{1o}^2 R_{eo}^2 \cos(2\omega t). \tag{3}
\]

Using Ohm’s law along with Eq. (3), the voltage across the probe wire can be written as

\[
V(t) = I(t)R_e(t) = \left[ I_1R_{eo} + \frac{3}{4} aZoR_{eo}^2 J_{1o}^2 \right] \sin \omega t - \left[ \frac{1}{4} aZoJ_{1o}^2 R_{eo}^2 \right] \sin 3\omega t. \tag{4}
\]

Equation 4 shows that the measured voltage is the combination of the \( 1\omega \) and \( 3\omega \) frequency harmonics of the initial heating current. A lock-in amplifier is used to selectively measure the RMS voltage corresponding to either component. The reported MWCNT data in the present study utilizes the \( 3\omega \) detection, since the constant ohmic signal contained within the \( 1\omega \) signal is expected to lead to a greater degree of scatter. In terms of the RMS voltage, the voltage at the third frequency harmonic, \( V_{3o,RMS} \), can be written as

\[
V_{3o,RMS} = \frac{1}{2} aZoJ_{1o,RMS} R_{eo} Q_{RMS}. \tag{5}
\]

where \( Q_{RMS} \equiv J_{1o,RMS} R_{eo} \). Dividing both sides of Eq. (5) by \( I_{1o,RMS} \), the RMS electrical resistance, defined as \( R_{e3o,RMS} \equiv V_{3o,RMS}/I_{1o,RMS} \), can be written as

\[
R_{e3o,RMS} = \frac{1}{2} aR_{eo} Zo Q_{RMS}. \tag{6}
\]

Next, the thermal transfer function \( Z_o \) is experimentally determined by obtaining the slope of \( R_{e3o,RMS} \) versus \( Q_{RMS} \). Since \( Z_o \) is a function of the sample thermal resistance, \( R_{th,S} \), and the probe-wire thermal resistance, \( R_{th,P} \), comparing \( Z_o \) with model predictions (see Sec. III B) for Joule heating in the probe wire with and without the sample allows both \( R_{th,P} \) and \( R_{th,S} \) to be determined.

### B. Analytical model for the thermal transfer function \( Z_o \)

The steady state thermal response of the probe wire is modeled using

\[
kp \frac{d^2 \theta(x)}{dx^2} = -\frac{Q_{RMS}}{ApLp}, \tag{7}
\]

where \( x \) is the coordinate along the length of the probe wire (Fig. 1), \( kp \) is the thermal conductivity of the probe wire, \( Lp \) is the length of the probe wire, and \( \theta(x) \) is the spatial temperature rise in the wire. Convection and radiation heat losses can be taken to be negligible, since the measurements are made using very small heating amplitudes in vacuum conditions within the SEM. (Using an analytic, 1D, steady state model to represent a 1-mm Pt probe wire having an average 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.)

The thermal resistance of the sample, \( R_{th,S} \), is incorporated into the model by a flux boundary condition at the point of the sample attachment, i.e.,

\[
\frac{\theta(0)}{R_{th,P}} = kpAp \left( \frac{\partial \theta(x)}{\partial x} \bigg|_{x=0^+} - \frac{\partial \theta(x)}{\partial x} \bigg|_{x=0^-} \right). \tag{8}
\]

The boundary conditions at the ends of the probe wire are

\[
\theta(+Lp/2) = \theta(-Lp/2) = 0. \tag{9}
\]

The piecewise parabolic solution for positive and negative \( x \) satisfying Eqs. (7), (8), and (9) can be expressed as

\[
0(x, \eta) = \frac{Q_{RMS}Lp}{8kpSp} \left[ \left( 1 - \left( \frac{x}{L/2} \right)^2 \right) + \left( \frac{\eta}{1+\eta} \right) \left( \left| \frac{x}{L/2} \right| - 1 \right) \right]. \tag{10}
\]

where the parameter \( \eta \) is the ratio of the thermal resistance of the probe wire to the thermal resistance of the sample \( R_{th,S} \) and is defined by \( \eta \equiv R_{th,P}/4R_{th,S} \). The thermal resistance of the probe wire and the sample is given by \( R_{th,P} = Lp/kpAp \) and \( R_{th,S} = Lp/kpAs \) respectively. In the absence of the sample, \( \eta = 0 \), resulting in the inverted parabolic solution of a Joule-heated suspended wire to be recovered from Eq (10).

Integrating over the length of the probe wire, the spatially averaged temperature rise \( \bar{\theta} \) of the probe wire can be written as

\[
\bar{\theta} = \frac{1}{12} Q_{RMS}R_{th,P} \left( 1 - \frac{3}{4} (1 + \eta^{-1})^{-1} \right). \tag{11}
\]

Comparison of Eq. (11) and (2) reveals the theoretical thermal transfer function to be

\[
Z_o = \frac{1}{12} R_{th,P} \left( 1 - \frac{3}{4} (1 + \eta^{-1})^{-1} \right). \tag{12}
\]

### C. Experimental procedure

Inserting Eq. (12) into Eq. (6) and taking \( \eta = 0 \) (absence of sample), the thermal resistance of the probe wire is first estimated using

\[
R_{th,P} = \frac{24}{2R_{eo} \Delta Q_{RMS}} \left( \frac{\Delta R_{e3o,RMS}}{\Delta Q_{RMS}} \right)_{No \ Sample}. \tag{13}
\]

As an aside, replacing the probe wire with a sample of unknown thermal resistance permits the thermal resistance and, therefore, thermal conductivity of the sample to be determined using Eq. (13). The caveat is that the sample’s electrical resistance and temperature coefficient of resistance must be known \textit{a priori}.\textsuperscript{1,17,18}

Next, the sample is attached and the new slope of \( R_{e3o,RMS} \) versus \( Q_{RMS} \) is measured. Calculating the ratio of the slopes \( \varphi \), where \( \varphi \) is defined as\textsuperscript{5}
The thermal resistance of the sample is found using

\[ R_{th,S} = \frac{1}{4} R_{th,p} \left( \frac{1}{4} a^{-1} - 1 \right), \]  

where \( a = 1 - \phi. \)

The sample’s thermal conductivity can be determined from its thermal resistance by using the relationship \( k_s = L_s/d \) (\( R_{th,S} \)), where the sample’s cross-sectional area is assumed, \( A_s = \pi (r_o^2 - r_i^2). \) In the present study, the inner radius, \( r_i, \) is approximated using the ratio of the average inner to outer radius, \( r_o, \) supplied per batch by both sample manufacturers.

D. Heater/sensor device for in situ SEM testing

The heater/sensor probe wire device used in the study is fabricated from commercially available Wollaston wire (Sigmund-Cohn Corp., Mt. Vernon, NY) composed of a 75-μm silver sheath surrounding an approximate 500–750-nm platinum core. A concentrated nitric acid solution is used to selectively etch the silver sheath, exposing the Pt core (Fig. 2(a)).

![Image](72x128 to 276x434)

**FIG. 2.** (Color online) Images of sensor package (a) during the Wollaston etching process. The package contains two removable chipsets. Each chipset has two Wollaston probe wires marked 1–4. Each Wollaston wire is labeled (a). The Wollaston wires are shown connected to copper contact pads using an electrically conductive silver epoxy. Label (b) marks the droplet of nitric acid on the Teflon spoon used to etch the Ag clad from the Wollaston to reveal the Pt core. (b) The sensor package mounted inside the SEM chamber with micromanipulators marked (c) and SEM stage marked (d).

To increase throughput, the entire measurement system comprises of four etched Wollaston wires labeled (a) in Fig. 2(a). Only one probe wire is utilized per experiment. A custom switch-box is used to independently activate each wire (not shown). The device comprises four probe wires with nearly the same average diameters, but with varying lengths and, thus, with different thermal resistances. Figure 2(b) shows the four probe wires mounted inside the SEM chamber (FEI FE NanoSEM 600). All the 4 probe wires are reachable by nanomanipulators inside the SEM chamber.

E. Probe wire thermal resistance and sensitivity

The length of the exposed platinum core and, thus, the thermal resistance of the probe is readily controlled by carefully maneuvering the droplet of nitric acid during the etch process. This permits the sensitivity of the probe to be maximized relative to the sample being tested.

The relative uncertainty in the measured temperature, \( \frac{\delta \theta}{\theta} \), is taken to be 0.005 (inferred from the linear regression of \( R_{th,S, RMS} \) versus \( QRMS \) using the experimentally determined temperature coefficient of resistance of the probe wire \( a \approx 0.0033 \) and maintaining the average temperature rise of the probe wire at \( \theta \approx 10 \) K). As per the analysis of Dames et al., the ratio of \( \delta \theta/\theta \) to the specifiable maximum relative uncertainty in the sample thermal resistance, \( \delta R_{th,S}/R_{th,S} \), is the sensitivity factor,

\[ s = \frac{\delta \theta/\theta}{\delta R_{th,S}/R_{th,S}}. \]  

If the uncertainty in the measured sample thermal resistance is taken be \( \delta R_{th,S}/R_{th,S} = 0.10, \) Eq. (16) is readily solvable using Eq. (11) for the maximum and minimum values of \( \eta, \) which provides the required sensitivity. Negating the effects of thermal contact resistance at the probe-sample interface, the maximum probe sensitivity occurs when the probe and sample’s thermal resistance is \( \eta = 1. \) The uncertainty in the measured sample thermal resistance will be within 10% of its true value if \( \eta \) is between 0.077 and 12.923. The average thermal resistance of all prepared Wollaston wire probes used in this study is \( 4.02 \times 10^7 \pm 1.15 \times 10^7 \) W/K. Therefore, samples having thermal resistances (intrinsice plus TCR) as high as \( 5.20 \times 10^8 \) W/K and as low as \( 3.11 \times 10^7 \) can be measured to within a confidence of 10%.

F. Method validation

The experimental analysis and equipment setup is verified by both a \( \omega \) and \( 3\omega \) self-heating experiment on 99.99% Au wire. The Au wire is chosen for its uniformity of diameter (3.4% variation) over the etched Wollaston probe wire, which has an average 17% variation in diameter. The \( \omega \) and \( 3\omega \) Au self-heating validation experiments result in a 2.3% and 3.6% difference from the literature value (306.6 W/m-K), respectively.

The use of the suspended Pt wire as a thermal resistance sensor is also validated (Fig. 3). A separate length of etched Wollaston wire is soldered to a nanomanipulator and treated as a sample of unknown thermal conductivity. To maximize
the thermal resistance per unit length of the Pt-probe, measured using Eq. (15), the thermal contact resistance (TCR) at the EBID reinforced probe-sample interface is determined to be negligible.

Prior to applying the Pt-EBID, the perceived sample’s thermal resistance (sample plus contact) is 2.9 times greater, which emphasizes the importance of improving the thermal contacts, especially as sample diameters decrease. Depending on the contact area, MWCNTs have diameters approximately 3% to 5% of the etched Wollaston Pt wire and may have a TCR of the same order as the intrinsic thermal resistance of the MWCNT samples. Values of TCR between the MWCNT samples and the Pt-probe are quantitatively analyzed in Sec. IV B.

III. MWCNT SAMPLES

Two sample groups are investigated in the present study: 1) MWCNT samples synthesized via thermal CVD and 2) MWCNT samples synthesized via thermal CVD and subsequently heat-treated at 3000 °C for 20 h (thermal annealed). The heat-treated thermal CVD MWCNT samples are acquired from US Nanomaterials Research (US4400, US4406, and US4412). The second set of samples, termed “non-heat-treated”, are comprised of thermal, CVD-grown MWCNTs purchased from US Nanomaterials Research (US4309 and US4315) and NanoLab (PD15L5-20). The NanoLab samples were synthesized at 600 ± 15 °C, and all US Nanomaterials Research samples were grown at 665 ± 15 °C.

The samples tested have a high degree of variation in diameter, shape, length, and straightness. Comparison of Figs. 4(a)–4(c) and/or Fig. 4(e) indicates that the high temperature heat treatment process promotes bonding among adjacent MWCNTs leading to the formation of multiple junctions and/or branching (Fig. 4(b)). Once selected using a manipulator probe, a greater majority of heat-treated samples have debris attached to the outside sample walls when compared to the non-heat-treated MWCNTs. Also, the heat-treated batches (US4309 and US4315) have a higher degree of abrupt changes in angle (Figs. 4(c) and 4(d)) compared to the PD15L5-20 batch (Figs. 4(e) and 4(f)). The source of these angle changes is likely due to defects in the lattice structure of the CNTs.7

A. Raman spectroscopy

Raman spectroscopy (514-nm excitation wavelength) is used to validate the improvement in graphitization and purity of the heat-treated sample batches compared to the non-heat-treated sample batches. An assessment of both residual amorphous carbon and defects is made by examining the ratio of the D band peak (~1350 cm⁻¹) intensity to the G band peak (~1580 cm⁻¹) intensity. The D band (defect band) is activated by carbonaceous impurities with sp³ bonding and also fragmented sp² bonds. These features are indicative of MWCNT defects.20 The G band is activated by contiguous sp² bonding, i.e., a high degree of graphitic crystallinity. Therefore, when comparing two sample groups, a smaller D/G band ratio is representative of a sample with
fewer defects and a higher degree of graphitization. To date, standards to quantify purities, diameters, wall numbers, and, most importantly, growth conditions of MWCNT samples have not been well established. Lacking a standardized MWCNT sample set, Raman spectroscopy remains a qualitative, yet effective, assessment of purity. It is important to note that the Raman laser, used to activate the phonon modes within the samples, has a spot size of ~1 μm. Therefore, the Raman data is an average response of not one specific MWCNT sample, but the group of samples exposed to the laser.

Figure 5 compares the Raman intensity of 3 non-heat-treated sample batches (US4309, US4315, and PD15L5-20) to the Raman intensity obtained from 3 heat-treated sample batches (US4400, US4406, and US4412). The Raman intensity is normalized to the maximum G band peak. Comparison of Figs. 5(a)–5(b) suggests that a significant amount of defect healing and graphitization has occurred in the heat-treated samples during the 3000 °C annealing process.

IV. RESULTS AND DISCUSSION

A. Thermal conductivity versus sample quality

On a sample-specific level, SEM images (including Figs. 6 and 7) are used to qualitatively categorize both the non-heat-treated and heat-treated samples into three main categories: samples with 1) minor defects; 2) moderate defects; and 3) severe defects. CNT side growth (branching) at angles to the main CNT tube axis have been previously shown to be caused by wall defects.7 Besides branching, the specimens in the present study also show abrupt changes in diameter as well as the presence of excessive surface debris. None of the selected specimens from either manufacturer are considered “flawless.” Not surprising, the mean thermal conductivity in specimens from the severe defects category is statistically less than those specimens from the moderate and minor categories. Samples described by the minor and moderate category are subsequently divided into heat-treated (Fig. 6) and non-heat-treated (Fig. 7) sample groups. The severe category comprises the sample group with morphological defects. In this manner, a filtering process was performed to identify samples having gross morphological deformities. Because these deformities are not uncommon in CVD-grown MWCNTs, reporting the thermal conductivity of such structures is important when determining the
thermal performance of similar commercially available nanomaterials.

A total of 29 measurements of MWCNT conductivity are performed. Six non-heat-treated and 15 heat-treated MWCNTs are measured to determine the effect of high temperature heat treatment on thermal conductivity. The mean thermal conductivities and Raman $D/G$ ratios of the non-heat-treated MWCNT samples provided by US Nanomaterials Research and the non-heat-treated MWCNT samples provided by NanoLab are found not to have a statistically significant difference. For this reason, both sample sets are placed into the same non-heat-treated sample group.

All non-heat-treated samples produce $D/G$ ratios that are approximately 3.3-fold greater than the heat-treated batches, indicating a significant presence of average defects and amorphous carbon content. Not correcting for an estimated value of TCR, Fig. 8 suggests that samples selected from the heat-treated batches produce a mean thermal conductivity nearly 5-fold times ($4.88 \times$) that of the non-heat-treated group ($216 \pm 149$ W/m-K and $44 \pm 29$ W/m-K,

![FIG. 6. SEM micrographs of experiments from the heat-treated sample set. In each case, the Pt probe wire is pictured above the manipulator tip, with sample joining the probe wire to the manipulator. (a) Highest measured thermal conductivity ($730 \pm 152$ W/m-K), statistically an outlier; (b) and (c) the two highest measured values of the heat-treated samples that are within the 20% confidence interval about the groups mean, $290 \pm 28$ W/m-K and $254 \pm 42$ W/m-K, respectively; (d) and (e) the two lowest measured values of the heat-treated samples, $80 \pm 16$ W/m-K and $67 \pm 11$ W/m-K, respectively. Note the values reported are prior to correcting for thermal contact resistance.](image)

![FIG. 7. SEM micrographs of experiments resulting in the two highest (a) and (b) and two lowest (c) and (d) measured thermal conductivity values of the non-heat-treated sample group. (a) $102 \pm 17$ W/m-K; (b) $61 \pm 6$ W/m-K; (c) $24 \pm 4$ W/m-K; (d) $21 \pm 9$ W/m-K. In each case, the Pt probe wire is pictured above the manipulator tip with sample joining the probe wire to the manipulator. Note the values reported are prior to correcting for thermal contact resistance.](image)

![FIG. 8. (Color online) Thermal conductivities not adjusted for thermal contact resistance plotted vs the ratio of the $D$ to $G$ Raman spectroscopy peaks as measured on each respective sample batch using a 514-nm excitation source. Error bars correspond to the standard deviation calculated from the variance of all samples within each sample group and do not reflect the measurement uncertainty.](image)
respectively). Note the large standard deviations are due to the variations in thermal conductivity within the group and do not reflect measurement uncertainty. Comparison of the non-heat-treated and heat-treated samples using a one-way analysis of variance resulted in a \( p \)-value of 0.015, indicating that the graphitization process has a statistically significant effect on the thermal conductivity of the samples. Due to the unique morphology of each sample tested, MWCNT thermal conductivity may be better evaluated on a more sample specific level. However, the mean thermal conductivity of all non-heat treated samples is found to be similar to CVD grown MWCNTs measured via the “self-heating” of 1-2-mm-long MWCNT bundles with estimated phonon mean free paths of a few nanometers.\(^{21}\) Phonon mean free path can be estimated by assuming that the thermal conductivity obeys the bulk expression \( k = \frac{1}{2} C v \lambda \),\(^{22}\) where \( k \) is the thermal conductivity, \( C \) is the specific heat, \( v \) is the phonon group velocity, and \( \lambda \) is the phonon mean free path. Considering a value of the specific heat of graphite at 293 K as \( 1.63 \times 10^6 \text{ J/m}^3\text{-K} \) and a Debye velocity of approximately \( v \approx 1.48 \times 10^7 \text{ m/s} \) (see Sec. IV B), the phonon mean free path of the heat-treated group is approximately equal to 20 nm, as compared to 5 nm for the non-heat-treated group. As discussed in Sec. IV B, the phonon dispersion relation for graphite accurately reproduces the specific heat of MWCNTs for temperatures greater than 10 K, suggesting that the specific heat and phonon group velocities of graphite may be used to evaluate phonon mean free path in MWCNTs near 273 K.

Because the phonon mean free path of the non-heat-treated sample group is estimated to be less than the average wall thickness of the samples (approximately ranging from 7–55 nm), a considerably greater degree of inter-wall scattering is likely to occur. Moreover, the measured thermal conductivities of the non-heat-treated samples are found to be similar to those values measured in similar-diameter vapor-grown carbon fibers.\(^{23}\) suggesting that similar phonon transport occurs in these fibers as in the non-heat-treated CVD-grown MWCNTs.

Prior to correcting for an estimated TCR, the highest measured thermal conductivity in the present study is \( 730 \pm 153 \text{ W/m-K} \) for a heat-treated sample having a measured outer diameter (OD) of 35 ± 4 nm, a 10.15 nm inner diameter (ID), and a length of 10.77 ± 0.04 \( \mu \text{m} \). Not surprisingly, this sample is the straightest of all samples measured and has the least number of visible physical defects (Fig. 6(a)). Using the prior argument, the average phonon mfp in this structure can be estimated to be approximately 60 nm, which suggests very little inter-wall phonon scattering, since the wall thickness is less than the estimated phonon mfp. Considering its straightness, the sample does not represent the majority of specimens tested.

Interestingly, all 8 samples having severe defects (not shown) are from the heat-treated sample group. The greater number of “kinks” in these samples is likely to reduce phonon mean free path, accounting for a reduced thermal conductivity. The sample group with severe defects is found to have a thermal conductivity of \( 50 \pm 28 \text{ W/m-K} \), where the reported standard deviation is due to the large variation of thermal conductivities within the group and does not reflect the measurement uncertainty. Since the sample group with severe defects consists of all heat-treated samples and has a mean conductivity similar to that of the non-heat-treated group, the reduction in thermal conductivity of these samples suggests that the gross physical deformities negate the effect of graphitization. As described by Ref. 7, heat treatment, even at high temperatures, such as 3000 °C, is unable to heal major defects. Therefore, it is likely these specific samples contained severe defects prior to heat treatment.

The measured thermal conductivities do not correlate well with sample outer diameters (Fig. 9). Outer diameter measurements may correlate to thermal conductivity, since smaller diameter tubes generally have fewer wall numbers, permitting less inter-wall phonon scattering.\(^{2}\) Following this reasoning, a single wall carbon nanotube has the highest theoretical thermal conductivity. If a correlation of thermal conductivity to diameter of the samples tested in the present study exists, the correlation is likely to be unnoticeable due to the variations in the structural quality. It has been proposed that shorter sample lengths may be responsible for a reduction in phonon mean free paths and, thus, apparent thermal conductivities.\(^{24}\) Similar to diameter, the measurement of sample length effects places a strict demand on sample quality.

The magnitude of the thermal conductivities reported in the present study are far below the highest measured MWCNT of approximately 3000 W/m-K.\(^{1}\) However, the variation of specimen quality makes comparison to other literature values especially difficult. Very little information is available on the quality and synthesis protocols of the tested MWCNTs reported in the literature. The mean thermal conductivity of the heat-treated sample group is in agreement with individual MWCNT measurements via self-heating.\(^{4}\) The variation in an individual MWCNT’s crystallinity and the amount of residual catalyst material in samples is likely to account for the wide variations in the reported literature values (Fig. 9).

![FIG. 9. (Color online) Thermal conductivity measurements of both heat-treated and non-heat-treated sample groups plotted against references (Refs. 1–4).](Image)
B. Estimating thermal contact resistance

In 2008, Prasher\textsuperscript{25} modeled the values of thermal conductivity of an individual 14-nm-diameter MWCNT between 10 and 100 K, as measured by Kim\textit{et al.}\textsuperscript{1} The experimental values were accurately reproduced by estimating the TCR at the two contact points between the MWCNT and the platinum-sensing device. The model for TCR used a diffusive mismatch model (DMM),\textsuperscript{26} which incorporated an approximate version of the phonon dispersion of graphite along with a Debye phonon model for platinum.

Because Prasher\textsuperscript{25} modeled the thermal properties of the MWCNT up to a temperature of only 100 K, he employed a semi-continuum version of the phonon dispersion relations (developed by Kumatsu\textsuperscript{27}). The dispersion relations assumed that all in-plane acoustic phonon modes were isotropic, allowing for a 2D density of states approximation to be used with a single Debye cutoff wavevector. Moreover, optical phonon modes were ignored, due to their low contributions at the temperatures of interest. It is to be noted that, in the past, Komatsu’s dispersion relations have also been used by Heremans and Beetz,\textsuperscript{23} Kelly,\textsuperscript{28} and Reynolds\textsuperscript{29} to calculate both the thermal conductivity and specific heat of graphite up to 100 K which was the temperature range of interest in the analysis by Prasher.\textsuperscript{25}

Specific heat per unit volume is determined by the rate of change of internal energy per unit temperature and is given by

\[ C = \frac{dU}{dT} = \frac{1}{V} \sum_{p} \sum_{k} \frac{df}{dT} \hbar \omega, \quad (17) \]

where \( V \) is the volume of the material, \( f = 1/ \left( \exp(\hbar \omega/k_B T - 1) \right) \) is the Bose-Einstein phonon distribution function, \( \omega \) is the phonon angular frequency, \( k_p \) is the phonon polarization index, \( k_B \) is the Boltzmann constant, and \( \hbar \) is the reduced Plank constant. Because the semi-continuum dispersion relations used by Prasher\textsuperscript{25} were isotropic in the graphene plane, using a 2D density of states relationship, Eq. (17) can be written as

\[ C = \frac{1}{(2\pi)^2} \sum_{\rho=1}^{3} \int_{k_{\rho}} \frac{df}{dT} \hbar \omega_{\rho} dk_{\rho}dk_{\rho}. \quad (18) \]

When applying the phonon dispersion relations used by Prasher\textsuperscript{25} to Eq. (18) and calculating for temperatures greater than 100 K, the specific heat of graphite is approximately 25% lower than measured values\textsuperscript{40} at 293 K. This indicates that either fully anisotropic phonon dispersion is required and/or optical modes have a significant contribution to the specific heat for nanostructures above 100 K.

There are two reasons why graphite dispersion should be adequate for estimating thermal properties of the large diameter MWCNTs investigated. First, a few studies have suggested that the out-of-plane elastic properties of MWCNTs are similar to graphite.\textsuperscript{21–33} Because MWCNTs lack the stacking order of graphite,\textsuperscript{25,33,34} the decreased interlayer coupling caused by the decreased stacking order is understood to result in reduced values of the out-of-plane elastic constants \( c_{13} \) and \( c_{44} \). However, the specific heat of graphite becomes increasing similar to that of graphene with increasing temperatures above 60 K,\textsuperscript{25} suggesting that interlayer coupling becomes less important with increasing temperatures.\textsuperscript{25,35}

The second reason why graphite dispersion may be used to estimate the thermal properties of the large diameter MWCNTs investigated is that the smallest of the nanotube diameters are not likely to interfere with the dominant phonon wavelength at 293 K. The dominant phonon wavelength can be estimated \( h v k_p \approx 2.6 k_B T \),\textsuperscript{28} where \( k_p \) is the dominant wave-vector. Assuming that the Debye velocity for the in-plane phonons is \( v = 1.48 \times 10^4 \) m/s, the dominant wave-vector is approximately \( k_p = 6.739 \) nm\(^{-1} \), which is equal to a wavelength of approximately 0.932 nm. In the present investigation, the inner diameters are relatively small. As provided by the manufacturer, the ID to OD ratio is likely in the range from 0.1 to 0.4. If \( k_p r = 1 \), where \( r \) is the nano-tube inner radius, the dominant phonon wavelengths in the nanotube will be much smaller than any of the nanotube inner circumferences. The smallest nanotube inner radius in the present study is estimated to be 2.5 nm; therefore, \( k_p r \approx 17 \). From this analysis, phonon confinement is not believed to exist in the rather large diameter samples investigated, and the phonon dispersion relation of graphite will likely be adequate. However, because the measurements are performed at 293 K, an accurate estimate of the TCR between the MWCNT samples and the EBID material will require a fully anisotropic complete set of phonon dispersion branches.

In the present study, a complete set of phonon dispersion relations is computed using molecular dynamics\textsuperscript{36} coupled with the second generation Tersoff-Brenner potential\textsuperscript{37} having a Lennard-Jones term to describe long-range van der Waals interactions. A 25 \times 25 \times 6 unit cell structure having an ABAB stacking order is built. The system is brought to equilibrium using 10 ps of integration using a microcanonical ensemble that maintains a constant total energy (NVE), followed by 10 ps of integration using a canonical ensemble (NVT) that brings the atoms in the system in equilibrium with a thermal reservoir to reduce the system temperature to \( 1 \times 10^{-10} \) K. A final 10 ps of NVE integration is subsequently performed. A reference unit cell containing 4 carbon atoms, \( i = 1 \) to 4, is chosen in the center of the structure. Each atom in the reference cell (labeled 0) is displaced by \( u_{\alpha} = 0.01 \) Å along the three Cartesian directions, \( \alpha = 1, 2, \) and 3. The resulting forces on every \( j^{th} \) atom in the \( n^{th} \) unit cell is measured in the \( \beta = 1, 2, \) and 3 directions. Because the system remains near equilibrium, the total system’s potential energy, \( U \), can by described by the Taylor expansion,

\[ U = U_0 + \sum_{i,0} \sum_{\alpha} \frac{\partial U}{\partial u_{\alpha}} \bigg|_{0} u_{\alpha} + \frac{1}{2} \sum_{i,0} \sum_{j,n} \sum_{\alpha,\beta} \frac{\partial^2 U}{\partial u_{\alpha} \partial u_{\beta}} \bigg|_{0} u_{\alpha} u_{\beta} + \cdots. \quad (19) \]

The first derivative of the system’s potential energy with respect to the small displacement of the \( i^{th} \) atom in the reference cell in the \( \alpha \) direction is equivalent to the negative
where a force constant matrix is defined as

\[ M_{ij} = \frac{\partial^2 U}{\partial x_i \partial x_j} \]  

which is the element of the mass matrix \( M \) labeled 0 in the reference cell. The Taylor series expansion at the second order term is known as the harmonic approximation and is increasingly valid near equilibrium conditions.

In the case of a plane wave traveling through the crystal in the \( k \) direction, the equation of motion of the \( i^{th} \) atom in the reference cell (labeled 0) with mass \( m \) (the element of mass matrix \( M \)) can be written as

\[ M_{ij} u_i^{(0)}(t) = -\sum_{jn} \Phi^{ij}(n) \bullet u_j^{(n)}(t), \]

where a force constant matrix is defined as

\[ \Phi^{ij}(n) = \frac{\partial^2 U}{\partial x_i \partial x_j(n)} \left|_{0} \right. \]

Solutions of plane waves having the form

\[ u^{i,0}(t) = \frac{1}{M^{1/2}} a(i, k, p) \exp(i[k \bullet r^{i,0} - \omega(k, v)t]) \]  

are sought, where \( a \) is the polarization vector and \( r^{i,0} \) is the position of the \( i^{th} \) atom. Dispersion relations are determined by solving the eigenvalue equation formed from substituting Eq. (22) into Eq. (20),

\[ \omega^2(k, v)a(k, p) = \left[ \frac{1}{M} \sum_{jn} \Phi^{ij}(n) \right] \exp(i[k \bullet (r^{i,0} - r^{j,0})]) \]

Equation (23) has a form where the mode frequencies squared are the eigenvalues and the polarization vectors are the eigenvectors. Force values are exported to a custom MATLAB script to calculate the 3 \( \times \) 3 force constant matrices between the reference cell and every \( n^{th} \) unit cell. Subsequently, eigenvalues of the 12 \( \times \) 12 Hermitian matrix are found for a particular wavevector \( k \).

The calculated phonon dispersion relations along the edges of the irreducible Brillouin zone are shown by Fig. 10. The dispersion relations generated by molecular dynamics using the 2nd generation Tersoff-Brenner potential \(^{37} \) reproduce the phonon dispersion obtained by inelastic neutron \(^{38} \) and x-ray scattering experiments \(^{39,53} \) reasonably well. Compared to experimental values, the MD dispersion model does produce harder frequency optical phonon modes in the in-plane direction. Similar to lattice dynamic models, the increased frequencies are expected, since the MD model measures lattice forces at 0 K, as compared to experimental measurements at room temperature. \(^{40} \)

To validate that the calculated phonon dispersion of graphite is adequate to model the thermal properties of MWCNTs at temperatures greater than 100 K, values of specific heat are estimated from the calculated phonon dispersion and compared to measured values of both the specific heat of graphite and MWCNTs. Because the phonon dispersion relationship is fully anisotropic within the irreducible
Brillouin zone (Fig. 10(b)), Eq. (17) can be recast in the form

\[
C = \frac{1}{(2\pi)^3} \sum_{p=1}^{12} \sum_{k_1,k_2,k_3} f \hbar \omega \Delta k_1 \Delta k_2 \Delta k_3, \tag{24}
\]

where \( \Delta k_1, \Delta k_2, \) and \( \Delta k_3, \) are interval spacing between a wavevector mesh established within the first Brillouin zone. Values of the integrand of Eq. (24) are computed at each grid point and for each of the 12 phonon polarizations.

The calculated values of graphite specific heat accurately predict the experimental values of both graphite and 10–20-nm-diameter MWCNTs to within 1% between 10 and 200 K (Fig. 11). The error slightly increases to approximately 3.3% at 293 K, likely due to the phonon population of the more inaccurate higher frequency optical phonon branches with increasing temperatures. Refinement of the interatomic potential or larger MD unit cell size may better capture the phonon dispersion of graphite, the phonon dispersion relations in the present study predict the specific heat of graphite with great accuracy as compared to two-dimensional density of state approximations.

The thermal contact conductance between the MWCNT sample and the EBID material is determined for the geometries shown in Fig. 12. Trimethyl-platinum-methylcyclopentadienyl (Me3PtCpMe) is used as the Pt deposition precursor. Without post-deposition treatment, metal-organic precursor materials typically deposit less than 50% Pt when using a focused electron beam. Me3PtCpMe is known to deposit anywhere between 10–15% Pt, with the rest being comprised of large amounts of carbon and oxygen from non-dissociated precursor fragments and residual carbon-based contamination originating from the vacuum chamber. Deposited Pt structures have been shown to consist of polycrystalline aggregates of 2 nm average diameter immersed in an unstructured carbon matrix. For this reason, two scenarios are investigated in the analysis of TCR. First, the EBID is assumed to be 100% Pt, and in the second, a 100% amorphous carbon material. In both circumstances, a Debye model is assumed within the EBID material. The assumption of isotropic dispersion is valid, since the EBID material is likely to be disordered. Nanoindentation tests have found that the measured elastic modulus of EBIDhydrogenated amorphous carbon deposits from paraffin precursors is dependent on the e-beam deposition voltage. In the present study, a value of 40 Gpa for Young’s modulus and a Poisson’s ratio of 0.25, as measured from hydrogenated amorphous carbon films, is used to calculate a Debye velocity of 3380 m/s; the Debye cutoff wave vector is estimated using \( k_D = \left[ \frac{6\pi^2 N/N}{V} \right]^{1/3} \), where \( N/V \) is the number of atoms per unit volume of substance.

In both circumstances, the EBID material is assumed to make perfect physical contact with the sample over half the sample diameter (Fig. 12). Because EBID is a form of chemical vapor deposition, surface undulations in the sample and on the Pt probe wire are likely to be filled with material. Assuming a van der Waals attraction between a cylinder and a perfectly flat substrate, the contact width, \( b \), is estimated from the elastic properties of the sample and substrate material. The analysis of contact width, including all material parameters, can be found in Ref. 25. For every sample tested, the contacting perimeter at the EBID and sample interface is assumed to be \( \pi D_s/2 \), where \( D_s \) is the outer diameter of each sample tested. The contacting perimeter is approximately 10–17 times greater than the calculated contacting widths, \( b \). Because the majority of the contacting surface is between the sample and EBID material, the EBID material is assumed to have a total contact area of \( A_c = L_c \left( \pi D_s/2 + b \right) \), where \( L_c \) is the contact length, as measured using the SEM (Fig. 12). Each contact area is calculated per experiment. The TCR is determined between the sample and EBID. The thermal boundary resistance between the EBID and the substrate is neglected, because the contact area between the EBID and substrate is significantly greater than the contact area between the EBID and sample.

According to the DMM model, the flux in the sample can be written using the properties of the sample and a transmissivity function, \( \tau_{1-2} \), describing the ratio of energy transmission from the sample to the EBID. If the difference in temperature across the interface is small, the thermal boundary resistance, \( R_b \), expressed as conductance per unit area of contact (WK\(^{-1}\) m\(^{-2}\)) between the sample and EBID can be expressed in the form of a contact boundary conductance written as

\[
G_b = \frac{1}{R_b} = \frac{1}{2} \left( \frac{1}{2\pi} \right)^3 \sum_{p=1}^{12} \sum_{k_1,k_2,k_3} \frac{d}{df} (\tau_{1-2} f) \hbar \omega \Delta k_1 \Delta k_2 \Delta k_3, \tag{25}
\]

where \( \nu_{f,z} \) is the group velocity in the z-direction measured by differentiating the phonon dispersion curve at each \( k_z \) point. The DMM model is used along with the gray medium approach to calculate \( \tau_{1-2} \).

![Fig. 12. (Color online) Schematic of contact configuration between the MWCNT (sample) and the Pt probe wire or nanomanipulator probe (substrate). Electron beam–induced deposition (EBID) of a Me3PtCpMe precursor is assumed to completely cover half of the sample circumference (\( \pi D_s/2 \)).](image-url)
The summation index of 3 in the terms corresponding to the EBID material represent three phonon polarizations. The calculated contact conductance suggests that the amorphous carbon EBID material increases the contact conductance by 17% compared to the pure Pt-EBID (Fig. 13).

At 293 K, the Pt-EBID and the amorphous carbon EBID are determined to have a contact conductance of 170.5 MWm$^{-2}$K$^{-1}$ and 190.5 MWm$^{-2}$K$^{-1}$, respectively. These values are equivalent to boundary resistance values of $R_b = 5.79 \times 10^{-9}$ Knm$^{-2}$W for the Pt-EBID and $R_b = 5.18 \times 10^{-9}$ Knm$^{-2}$W for the amorphous carbon EBID, which are consistent with theoretical estimates and experimental data for some interfaces.

The temperature in the portion of the MWCNT sample in contact with the EBID material is a function of the contact length, $L_c$; therefore, this portion of the sample experiences additional thermal resistance analogous to an extended fin, which is either being heated or cooled by a surrounding media. Since the experiment is performed under vacuum conditions, the effective fin perimeter is taken as $P = \pi D_f/2 + b$ and the fin heat transfer coefficient is $h = 1/R_b$, where $R_b$ is calculated using Eq. (25). Applying an adiabatic tip condition, the effective thermal resistance of both contacts is written as

$$R_{TCR} = \frac{2}{\sqrt{hP_kA_s} \tanh\left(L_c \sqrt{\frac{hP_k}{k_sA_s}}\right)}, \quad (27)$$

where $k_s$ is the axial thermal conductivity of the MWCNT sample and the factor of 2 takes into account both the EBID sample contact on the Pt thermal resistance probe wire and the manipulator.

The T-type hot wire probe measures a net thermal resistance (Eq. (15)),

$$R_{Total} = \frac{L_s}{k_sA_s} + \frac{2}{\sqrt{hP_kA_s} \tanh\left(L_c \sqrt{\frac{hP_k}{k_sA_s}}\right)}. \quad (28)$$

To estimate the effect of thermal contact resistance on the perceived values of thermal conductivity, Eq. (27) is subtracted from the measured thermal resistance (Eq. (15)). However, since a value of thermal conductivity is required to estimate the TCR, the value of thermal conductivity calculated from ignoring contact resistance is used as an initial guess, and improved values of thermal conductivity are iteratively obtained from Eq. (28). The fin resistance contribution to TCR has previously been shown to accurately model the measured thermal conductivity of MWCNTs resting on Pt substrates for temperature between 10 and 100 K, but has not been extended to EBID interfaces.

In the present study, adjusting the measured values of thermal conductivity using an estimated value of TCR is found to increase the reported values of thermal conductivity by approximately 5%, regardless of whether the EBID material is composed of pure platinum or amorphous carbon. Figure 14 shows the adjusted thermal conductivity values (open symbols) and the non-adjusted values (closed symbols) for the case of a Pt-EBID. The heat treated samples are found to have a greater increase in adjusted thermal conductivity, because these samples have less intrinsic thermal resistance.
and, therefore, the TCR is a greater fraction of the total measurement.

Interestingly, the majority of the thermal contact resistance for each sample originates from the “fin resistance” term. For example, the sample with the highest measured thermal conductivity has a measured total thermal resistance $R_{\text{total}} = 1.66 \times 10^{-7}$ K/W. Considering the sample outer diameter $D_o = 35$ nm, the calculated contact width $b = 4.2$ nm, and a contact length $L_c$ of 732 nm, the estimated contact area is $4.332 \times 10^4$ nm$^2$. A value of TCR that excludes the fin resistance results in an estimated thermal contact resistance of $2.82 \times 10^5$ K/W, which is less than 1% of $R_{\text{total}}$, while $R_{\text{TCR}}$ from Eq. (27) is $7.83 \times 10^5$ W/K, which is 4.7% of $R_{\text{total}}$.

The importance of including fin resistance when estimating TCR is shown in Fig. 15. In the previous example, values of $R_{TCR}$ are compared to the contact resistance calculated by omitting the fin resistance ($R_{\text{fin}}/A_c$) for extrapolated values of $L_c$ and $D_o$. For small contacting lengths of EBID, the TCR is shown to be more sensitive to $L_c$ and $R_{\text{fin}}/A_c$ gives the same estimate as Eq. (27). For longer EBID contact lengths ($L_c > 100$ nm), TCR gradually becomes insensitive to $L_c$ and the TCR is dominated by the sample outer diameter. For smaller sample diameters, $D_o < 50$ nm, and EBID lengths of $L_c > 100$ nm, Eq. (27) provides a more conservative estimate of the total TCR.

The reductions in contact resistances that occur when using EBID result from increasing the contact area at the sample-probe and the sample-manipulator interfaces. The addition of mass should not affect the steady state temperature profile that develops in the experiment as long as the diameter of the Pt probe wire is not altered to interfere with the 1D heat assumption model. However, the addition of EBID mass is likely to help enforce the $\theta_0 = 0$ boundary condition at the manipulator-sample attachment point (Fig. 1).

C. Other sources of uncertainty

The largest source of experimental error lies in the measurement of sample diameter and the definition of an effective sample diameter. The SEM is capable of making repeatable diameter measurements within ±4 nm. Any variation in sample diameter will add to this uncertainty. Since thermal conductivity is a function of the sample cross-section area, the relative uncertainty in sample diameter, $\Delta D_o/D_o$, is doubled. The average relative uncertainty in sample diameter for all measured samples in this study is 9% and is dominated mostly by non-uniformity of sample diameter.

A finite difference model is used to predict the error caused by neglecting radiation heat loss by comparison of the governing heat equation of the Pt probe with and without the radiation term. For the geometries of probe wires used in the study, a 0.5% error is expected when neglecting radiation. Other uncertainties include sample lengths, $\Delta L/L$ (∼1%). (The reported relative uncertainty in sample length excludes the rejected sample group.) Room temperature probe electrical resistance, $\Delta R_{\text{res}}/R_{\text{res}}$ (<0.1%), and temperature coefficient of resistance of the probe, $\delta R/\rho$ (2.2%). Neglecting contact resistance, all uncertainties in conjunction with the aforementioned sensitivity calibration of the probe result in a relative measurement uncertainty of approximately 20%. This measurement uncertainty is believed to be symmetric about the mean, i.e., ±10% of the mean reported values.

Comparing the average 20% relative uncertainty in the thermal conductivity of each sample tested to the 71% variation about the mean of the heat-treated sample group and the 180% variation about the mean of the non-heat-treated sample group suggests that variations in sample quality within each sample group are significant. The large variations are likely due to wall and other morphological defects in the heat-treated group and both wall defects and residual Fe catalyst in the non-heat-treated group.

V. CONCLUSION

This study highlights the beneficial effects of high temperature heat treatment (∼3000°C) on the thermal conductivity of CVD-grown MWCNTs when compared to non-heat-treated CVD-grown MWCNTs. A nearly 5-fold increase in thermal conductivity is obtained for MWCNT samples, which undergo a 20-h 3000°C post-annealing heat treatment. However, in most samples, severe defects are found to negate any advantage of the heat treatment process.

TCR is estimated using a comprehensive anisotropic DMM model that uses complete dispersion relations calculated from force constant matrices obtained from MD. Phonon dispersion curves of graphite used to evaluate TCR accurately reproduce the values of MWCNT-specific heat...
for temperatures greater than 100 K. Subtracting the estimated TCR from the measured values of each sample’s thermal resistance results in an approximate 5% increase in thermal conductivity of each sample. Neglecting TCR results in comparatively little error when using EBID-reinforced contacts; however, samples with smaller intrinsic thermal resistance are shown to be more sensitive to errors caused by neglecting TCR. Because adjusting for TCR is independent of all the other measurement uncertainties, the mean reported values of thermal conductivity increase by approximately 5%. When EBID is applied to the contact point, the fin resistance resulting from the temperature gradient along the length of the sample in contact with the substrate and/or manipulator is found to be approximately 5 times more significant than the boundary resistance between the EBID and sample material.

Adjusting for TCR, the highest measured thermal conductivity is 765 ± 153 W/m-K. Variations in the physical structures of the sample are seen within each sample group and among each sample group, with the highest values of thermal conductivity being measured in the straightest heat-treated samples. The probe-sample thermal contact resistance may be explicitly measured by changing the length of the sample while maintaining the original probe-sample contact. As long as the magnitude of TCR is equivalent, comparisons between sample groups using a Wollaston thermal resistance probe are highly effective.

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APPENDIX I: FREQUENCY DEPENDENCE OF THE THERMAL TRANSFER FUNCTION

The heating current used to Joule heat the Pt probe is driven at a sufficiently low frequency to prevent a phase shift between the heating current and the temperature response. This is achieved by choosing a heating frequency whose period is less than the thermal diffusion time τ of a suspended wire, where τ = L²/α. The thermal diffusion time of the sensor wires is estimated to be approximately 0.02 s, which would require heating frequencies of less than 50 Hz. A 1 Hz heating frequency is used in the present investigation. To verify the operational frequency range of the experiment, the Pt probe wire is modeled as a 1D wire having constant cross-section area, A, length, L, density, ρ, and heat capacity, C. Homogeneous temperature boundary conditions θ(L, t) = θ(0, t) = 0 and initial condition θ(x, 0) = 0 along with Joule heating (current I1,oe²αt) is solved together with the time-dependent governing equation,

\[ \frac{\partial \theta(x,t)}{\partial t} = \frac{1}{\rho C_L} \frac{\partial^2 \theta(x,t)}{\partial x^2} + \frac{I_1,oe^{2\alpha t}}{\rho C_L}. \]  (A1)

Using the method of eigenfunction expansion, the spatially average series solution of Eq. (1) is written as

\[ \bar{\theta}(\omega) = \int_0^L \theta(x,\omega)dx = 4 \sum_{n=1}^{\infty} \frac{4}{\rho C_L} \frac{(1 - (-1)^n)(e^{2\alpha t} - e^{-(n\pi)^2t})}{(i2\omega + (n\pi)^2/\tau)}. \]  (A2)

The frequency-dependent thermal transfer function is then

\[ Z(\omega) = \frac{\bar{\theta}}{Q(t)} = \sum_{n=1}^{\infty} \frac{4}{\rho C_L} \frac{((-1)^n - 1)(e^{2\alpha t} - (n\pi)^2t - 1)}{i2\omega + (n\pi)^2/\tau}. \]  (A3)

Equation (A3) highlights the importance of minimizing the frequency to maintain the real part of the thermal transfer function and, thus, the measured 3rd harmonic voltage signal. The denominator of the last term of Eq. (A3) validates that longer Wollaston probe wires (larger L²/α) require lower frequencies to minimize the phase difference between the heating current and the thermal response. As frequency approaches zero, the steady state result utilized in Eq. (2) is recovered,

\[ Z(\omega \to 0) = 4R_{th,P} \sum_{n=1}^{\infty} \frac{(1 + (-1)^{n+1})}{(n\pi)^2} = \frac{R_{th,P}}{12} = Z_0. \]  (A4)

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