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OFF-AXIS THERMAL PROPERTIES OF CARBON NANOTUBE FILMS

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Theoretical calculations have predicted that individual Single-Walled Carbon Nanotubes (SWNT) have extremely high thermal conductivity (around 6.6×10^4 W/m-K). The feasibility of constructing practical devices using the above mentioned properties, is critically dependent on the ability to synthesize high-thermal-conducting films. Highly conducting films would be of great use as heat sinks for the next generation of integrated chips. Excessive heating is currently a very serious problem in the endeavor for achieving faster and smaller chips. Since it is still not possible to perfectly align SWNT in the macroscopic scale, the thermal properties of the nano-films are therefore expected to have a statistical effect and thus lower than the intrinsic thermal conductivity of a single nanotube. Also the thermal conductivity perpendicular to the tube direction is more significant from a practical point of view. Multi-Walled Carbon Nanotubes (MWNT) were synthesized by CVD technique and subsequently characterized. The thin MWNT films were deposited by a solution casting technique over a metallic substrate. The thermal properties of these nano-films were studied by AC- calorimetry studies. In this method, the sample is heated by an AC source and the measurement of the relaxation rate is used to determine the thermal properties. This technique is well established for studying the thermal properties of complex fluids. Our results are contrasted with other thermal conductivity measurements intrinsic and bulk carbon nanotube samples. To be best of our knowledge, this is the only off axis bulk thermal measurement reported on a MWNT film. A model to explain the thermal conduction for our system is proposed.

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1 Introduction

The physical properties of carbon nanotubes have intrigued scientists from the time of its inception in the 1990's. Its mechanical properties have been calculated to be stronger than steel [1], and it is predicted to challenge diamond in its thermal properties [2]. Its electronic properties also can be tuned from metallic to semiconducting depending on its structure [3]. Thus, it has been forecasted by many experts to be the "wonder-material" for the new century. However, its extremely small size makes the experimental verification of a number of these predicted properties on single intrinsic nanotubes very challenging. Electronic transport measurements have been performed [4] on Single-Walled Carbon Nanotubes (SWNT) and the results agree with theoretical predictions [5].

A number of electronic and micro-mechanical applications require the efficient conduction of heat in a microscopic and molecular level. Microscopic heating is the principal problem in the fabrication of a very high clock rate integrated circuit (IC) processor. The structure and properties of carbon nanotubes make it an ideal choice for future nano-scale circuits. Theoretical calculations using various models have predicted Carbon Nanotubes to have very high thermal conductivity. Molecular Dynamic Simulations (MDS) [6] have calculated the thermal conductivity of an isolated SWNT to be 6.6×10^4 W/m-K while phonon spectrum analysis [7] of SWNTs have found the thermal conductivity to be 6×10^4 W/m-K. Also, a modified empirical potential calculations [8] showed that the thermal conductivity of a few nanotubes to be 3×10^4 W/m-K. Experimental measurements on a lithographically fabricated single Multi-Walled Carbon Nanotube (MWNT) have yielded comparable results [9]. However, a majority of the carbon nanotube thermal applications will be using a large number of nanotubes and, most likely, as a thin film.

Thermal conductivity and specific heat are the two most important quantities necessary for fabricating future micro-thermal applications. A few direct experimental studies on carbon nanotube mats and bundles [10,11] have determined the thermal conductivity of the sample to be 10 to 100 orders of magnitude less than calculated values. These thermal conductivity measurements are all along the axis of the Nanotubes. The measurement reported in this article, determines the specific heat capacity and thermal conductivity perpendicular to the MWNT thin film using non-invasive AC calorimetry. At 300 K, the measured off-axis (perpendicular to the film) thermal conductivity was 1.5 W/m-K and the specific heat was 0.702 J/g-K .

2 Experimental Procedure

The Muti-Walled Carbon Nanotubes were synthesized by a Chemical Vapor Deposition (CVD) technique [12]. A schematic of the experimental set-up is shown in the Figure-1.

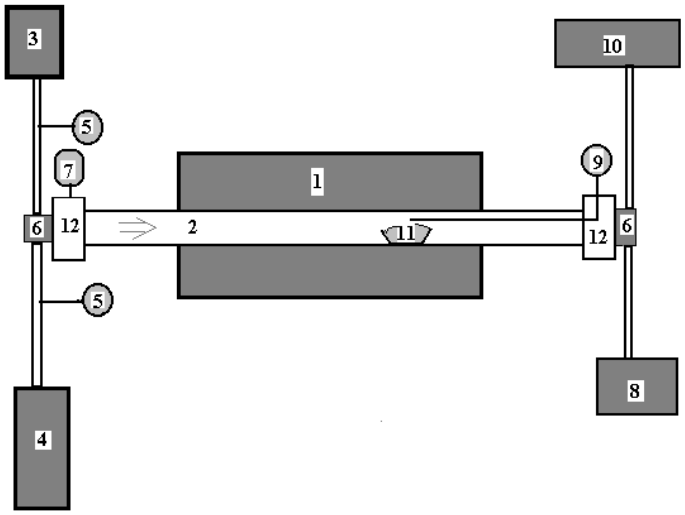

Figure-1: A schematic of the CVD set-up used for synthesizing the nanotubes: (1) Tube Furnace, (2) Quartz Tube, (3) Carrier Gas (Argon/Helium/Nitrogen), (4) Reactive Gases (Methane, Ammonia, Silane, etc.), (5) Flow controller/Meter, (6) 3-way Valve, (7) Pressure Gauge, (8) Vacuum Pump, (9) Thermocouple, (10) Gas Trap, (11) Catalyst, (12) Connector and Heating/Cooling coils.

A controlled and pre-determined mixture of Methane and Ammonia (Reactive Gas) mixed with inert Argon (Carrier Gas) was passed through a quartz tube inside a tube furnace (pre-heated to 873 K). Inside the tube, a ceramic boat containing Fe/Mo (Iron/Molybdenum) ultra-fine powder was heated. The commercially available 0.1 μm Iron/Molybdenum powder (Aldrich) was reground and put in the ceramic boat. The carbon from the reactive gases reacts with the catalyst particles to produce a Vapor-Liquid-Solid reaction leading to the formation of MWNT on the catalyst. About 1 g per hour of MWNTs was produced in the synthesis.

The synthesized nanotubes were subsequently imaged with an AFM (Digital Instruments Bioscope with a Nanoscope III controller) and SEM (ISI-DS-130). The AFM measurements were performed at Haverford College and the SEM images were obtained at Precision Combustion Inc. The sample was observed to have a distribution of tubes with three different diameters. There are a few thick tubes (diameter ~100 nm), some very thin tubes (diameter ~10 nm), and a majority of the tubes were ~30 nm in diameter. The latter are close to the diameters observed for standard MWNTs. The length of the tubes ranged from one to several microns. Prolonged sonication of the material did not reveal any appreciable change, indicating that the tubes to be isolated and did not form bundles. Figure-2 is a high-magnification AFM micrograph of a single MWNT. Figure-3 is a low-magnification micrograph of the film showing the distribution of nanotubes in the sample. Since the film was also prepared using the exact same procedure in preparing samples for these images, Figure-3 can also be considered an image of the film within the calorimeter.

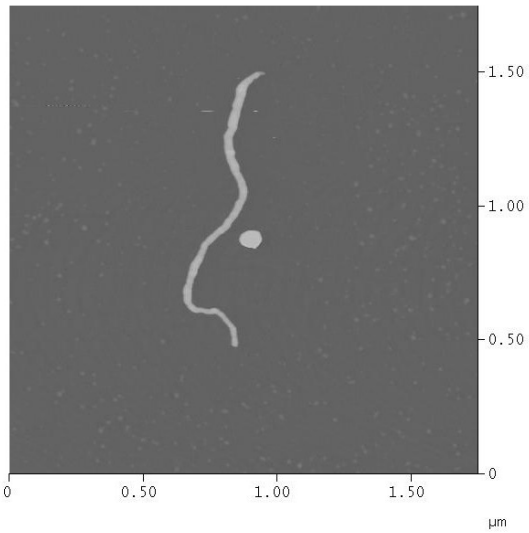

Figure-2: AFM Micrograph of a short single MWNT showing its thickness to be 30 nm and length to be 1µm . The images were collected in the "Tapping mode" at a frequency of 300 KHz with standard etched Si tips.

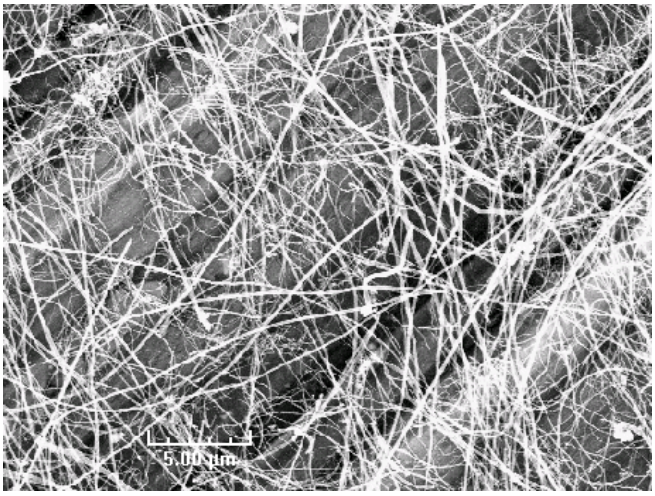

Figure-3: SEM micrograph of the nanotube film. The image was collected at a low magnification to have a larger field of view. The overall distribution of the nanotubes and a qualitative idea about the density can be observed. The SEM micrograph was collected at 15 kV

The thermal properties of a the nanotube film was studied by an AC calorimetric method. In this technique, the film and the substrate are subjected to an oscillatory heat. The specific heat and thermal conductivity can be determined by measuring the resulting temperature amplitude and frequency dependence, respectively. This method has a number of advantages. It requires a very small quantity of sample (ideal for films), has negligible radiative heat lost (good for temperature dependent measurements), directly

measures heat capacity, and is ideal for studying thermal properties of liquids and fluids --- especially at phase transitions. This method has been extensively used for the study of complex fluids and superfluid helium [13].

A small oscillatory heat input (power ~0.5 mW) supplied to the sample results in a modulated temperature having an amplitude T_{ac} (~5 mK), which is loosely coupled to a heat (thermal) bath. The amplitude T_{ac} is inversely proportional to the heat capacity of the sample. The amplitude is measured for an average temperature, which gives the temperature dependence of the heat capacity as the average temperature is changed. The specific experimental setup used is shown in Figure-4.

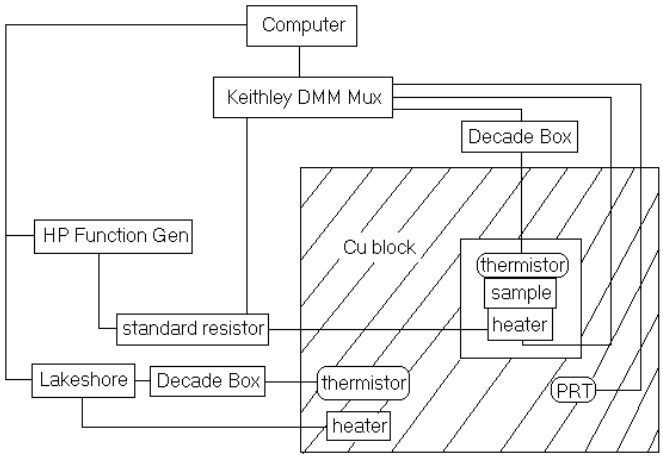

Figure-4: Schematic illustration of the AC Calorimetry set up used in this work at WPI.

The experiment is completely automated. The data taking algorithm begins when the computer instructs the Lakeshore temperature controller to ramp the temperature of the copper block at a set rate. It checks itself through measurements made of the thermistor. The decade box in parallel with the sample thermistor shown in Figure-4 merely lowers the excitation current going into the thermistor. The copper block acts as the thermal bath as discussed above. The function generator is instructed to output a sinusoidal voltage, through a standard resistor in series with a strain gauge heater attached to the bottom of the sample. This operating frequency is decided by studying the frequency response of the sample. The Keithley Digital Multiplexing Multimeter measures the voltage across the standard resistor to give the current and the voltage across the heater. The thermal power generated at the heater through Joule heating, is given by $P(t) = I*V = dQ_o/dt = P_o\, e^{-\omega t}$. As the bath is continuously ramped in temperature, the Keithley receives a trigger, digitizes the information (for a given number of points and rate corresponding to a set number of waveform periods), then transfers the data to the computer, which fits it to a sum of sine and cosine functions (including background terms to account for the ramped bath temperature). The coefficients of the sine and cosine term at the heating frequency determine the amplitude and phase of the temperature oscillations. The temperature oscillations of the nanotube film induced by the sinusoidal heating is given by

$$T_{ac} = \frac{P_0}{2\omega C}\left(1 + \frac{1}{\omega^2\tau_E^2} + \omega^2\tau_i^2 + \frac{2R_i}{3R_E}\right)^{-\frac{1}{2}} \quad (1)$$

where P_o the amplitude of the applied power, C is the total heat capacity of the sample+cell, ω is the angular heating frequency, τ_E and τ_i are the external (to the bath) and the internal (within the sample+cell) thermal relaxation times. The quantities R_E and R_i are the external and internal thermal resistances, respectively. The phase-shift between the heat input and the resulting temperature oscillation, $\Phi = \phi - \pi/2$, is given by

$$\tan\phi = \frac{1}{\omega\tau_E} - \omega\tau_i + \tan\phi_0 \quad (2)$$

The heat capacity can be closely approximated by Equation (1) at an operating frequency where the thermal relaxation and resistance are unimportant as $C \approx C^* \equiv P_o/\omega T_{ac}$. The thermal conductivity κ is determined by a frequency scan using both Equations (1) and (2), see Ref. [14] for details.

High-resolution AC calorimetry was performed using a home-built calorimeter at Worcester Polytechnic Institute. The sample cell consisted of a silver crimped-sealed envelope ~10 mm long, ~8 mm wide, and ~0.5 mm thick (closely matching the dimensions of the heater), which has attached a 120 Ω strain-gauge heater and a 1 MΩ carbon-flake thermistor. The sample (carbon nanotubes) was dissolved in high-purity acetone with a very low water content and the resulting 'solution' was introduced into a cell. The filled sample-cell was then placed in an ultrasonic bath to remix the sample, then the solvent was evaporated to form the film of nanotubes within the cell. Massing the cell before and after filling determined the sample mass. The sealed sample+cell was then mounted in the calorimeter. After collecting data, the specific heat is given by

$$C_p' = \frac{[C'_{filled} - C_{empty}]}{m_{sample}} = \frac{\frac{P_o\cos\phi}{\omega|T_{ac}|} - C_{empty}}{m_{sample}} \quad (3)$$

$$C''_{filled} = \frac{P_o}{\omega|T_{ac}|}\sin\phi - \frac{1}{\omega R_E} \quad (4)$$

where C_p' specific heat of the sample and C''_{filled} is the imaginary heat capacity (a measure of dissipative effects usually as a result of non-equilibrium conditions), C_{empty} is the heat capacity of the cell, m_{sample} is the mass in grams of the nanotube film (~1 mg), and R_E is the external thermal resistance. Equations (3) and (4) require a small correction to account for the finite internal thermal resistance R_i compared to R_E, and this was applied to the sample studied here. All data presented here were taken at frequency of 15.6 mHz at a scanning rate of ±2.3 K/h. The relative precision is 0.01%, however, the absolute precision is ~10% due to uncertainties in the applicability of the one-lump thermal model.

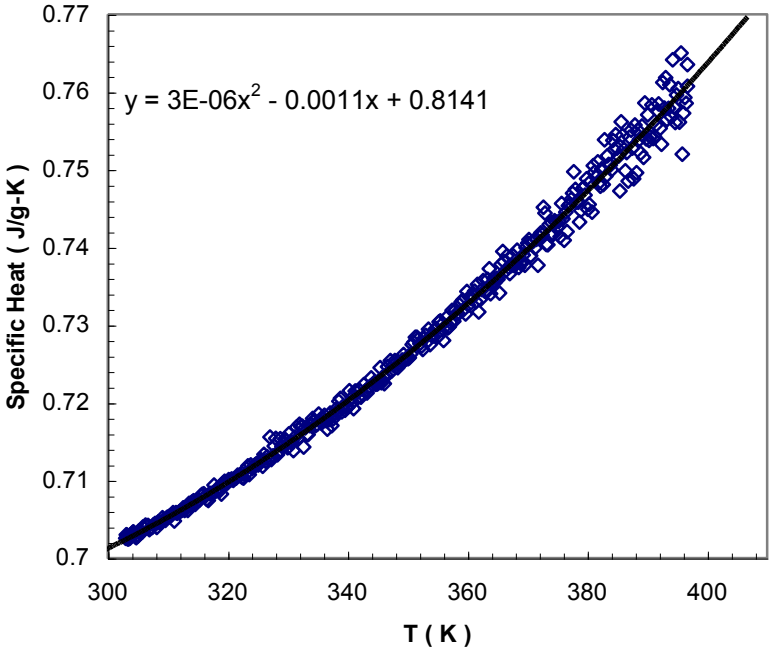

Figure-5: The dependence of Specific heat capacity of the film as a function of temperature from 300 to 400 K. The specific heat capacity increases about 10% in this interval. The increase is essentially linear with a small quadratic component. The fitting equation is shown on the top of the graph

3 Results and Analysis

The specific heat of the MWNT-based thin film was determined as a function of temperature from 300 to 400 K. The room temperature (300 K) specific heat was measured to be C_p = 0.702 J/g-K and is consistent with Ref. [10] and that found for graphite at room temperature. This is not surprising since MWNTs are formed with graphite-like C-C bonds. This C_p for MWNT is ~6 times less than that for water.

The specific heat and the thermal conductivity were both observed to be monotonically increasing with the temperature in the range studied. Theoretical calculations [6] on the thermal conductivity of an isolated SWNT predicts the thermal conductivity to be maximum around 100 K and then decrease. However, the mechanism of thermal conduction is more complicated for a thin film of a large number of randomly oriented nanotubes, as in the present sample. The intra-tube spacing will play a significant role in the thermal conduction than the nanotubes themselves. With a rise in temperature, the phonon modes increase, causing the spacing between tubes to decrease and, thereby, increase the thermal conduction. Experimental measurements on bulk

nanotube samples with other techniques [10,11,15] have also observed this trend. The 300 K thermal conductivity of the MWNT thin film was measured to be 1.5 W/m-K, which is 200 times less than the thermal conductivity for copper of 398 W/m-K at 300 K. This result is a lower than the thermal conductivity measurements by other groups [10] by almost a factor of 20 . The present measurement is different from the others as it measures the off-axis thermal conductivity of the MWNT. MWNTs are known to be anisotropic and a large difference is observed between its on-axis and off-axis electrical conductivities [16]. Thus our results are consistent with the electrical conductivities. To date this is the only off-axis thermal conductivity measurement reported.

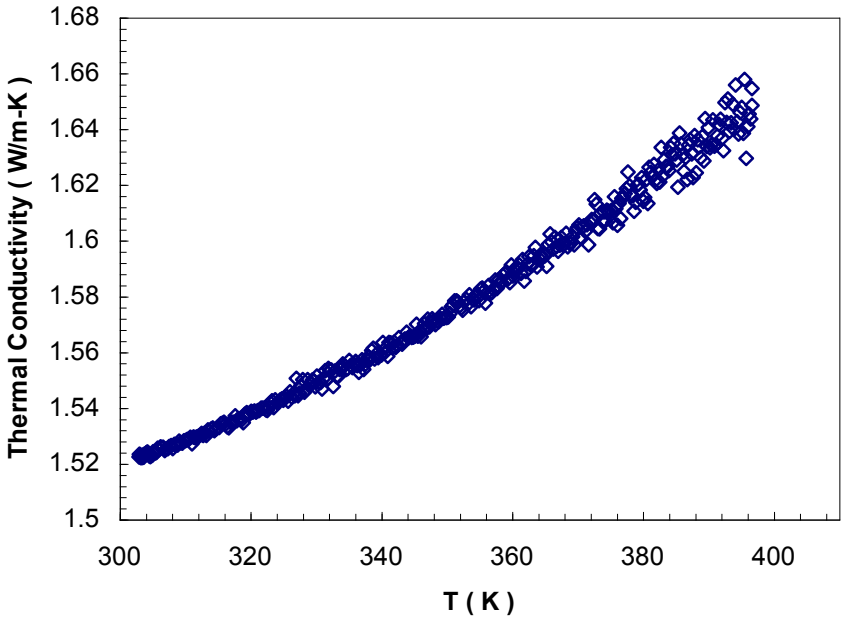

Figure-6: Temperature dependence of thermal conductivity. The room temperature value is κ = 1.5 W/m-K and increases by ~ 8% over a 100 K temperature rise.

An electronic system with elastic scattering (most metals) generally obeys the Wiedemann Franz law, $\kappa / \sigma T = L_o$, where κ and σ are the thermal and electronic conductivities while $L_o = 2.45\times10^{-8}$ W/Ω-K^2 is a constant for most materials. The constant L_o for a nanotube film is ~2.2×10^{-6} W/Ω-K^2, larger by a factor of 100 as observed in other measurements. This indicates that the off-axis heat conduction mechanism near room temperature is more metallic phonon-scattering, which is typically 100 times larger than electron scattering. In this case, the specific heat is determined from the standard phonon spectrum relation

$$C = \int_0^{\omega_{max}} k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}} \rho(\omega) d\omega}{\left(\varepsilon^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} \quad \textbf{(5)}$$

The experimentally determined $C_p(T)$ is nearly linear about room temperature, with a small quadratic component visible at higher temperatures, see Figure-5. This implies that the phonon density of states $\rho(\omega)$ is more or less constant within this temperature range. Also, since the Debye temperature for MWNT is much higher than our experimental region, we can treat this system as essentially one-dimensional. For a single MWNT, the conduction is dominated by the inter-tube geometry (cylindrical) and such a system can be considered 2-D. However, for a large number of randomly oriented tubes that constitutes a film, the intra-tube interaction consists of many point-like contacts (tubes touching, on average, at one point with each other). Such a system may behave more 1-D-like and possibly explain the discrepancy between thin film and isolated tube theoretical calculations. Also the current measurements are for heat propagation perpendicular to the tube which is much lower than the in-axis contribution.

If the system is treated as a classical 1-D phonon gas (valid for a large number of tubes), then the specific heat and the thermal conductivity are related by $\kappa = Cvl / 3$, where v is the phonon wave velocity in the MWNTs and l the mean free path. Using the values determined for the thermal conductivity and specific heat in this work gives a mean free path at room temperature of about $l \sim 0.2$ μm. The AFM micrographs were used to measure the height of the sample and for a majority of the samples it was measured to be close to 0.2 μm. However, this simple view is based on all tubes being homogenous and standing vertically on the surface, which is certainly not the case in our sample. Moreover the heat conduction was measured perpendicular to the tubes. So, this simplified model should be treated with caution.

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