TEMPERATURE AND FREQUENCY DEPENDENT
CONDUCTION MECHANISMS WITHIN BULK
CARBON NANOTUBE MATERIALS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

JOHN SIMMONS BULMER
B.S., UNITED STATES AIR FORCE ACADEMY, 2002

2010
Wright State University
I HEREBY RECOMMEND THAT THE THESIS
PREPARED UNDER MY SUPERVISION BY John
Simmons Bulmer ENTITLED TEMPERATURE AND
FREQUENCY DEPENDENT CONDUCTION
MECHANISMS WITHIN BULK CARBON
NANOTUBE MATERIALS BE ACCEPTED IN
PARTIAL FUILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF Master of Science.

____________________________
Gregory Kozlowski, Ph.D.
Thesis Director

____________________________
Lok C. Lew Yan Voon, Ph.D., Chair
Department of Physics
College of Science and Mathematics

Committee on Final Examination

____________________________
Jerry Clark, Ph.D.

____________________________
Benji Maruyama, Ph.D.

____________________________
Jason Deibel, Ph.D.

____________________________
Andrew T. Hsu, Ph.D.
Dean, School of Graduate Studies
ABSTRACT

Bulmer John Simmons, M.S., Department of Physics, Wright State University, 2010. Temperature and Frequency Dependent Conduction Mechanisms Within Bulk Carbon Nanotube Materials.

The resistance of three types of bulk carbon nanotube (CNT) materials (floating catalyst CNT yarn, forest grown CNT yarn, and super acid spun CNT fiber) was measured from room temperature to 900 C. Fitting the curves to established conduction equations for disordered materials, competing conduction mechanisms pertaining to the material could be determined. Floating catalyst CNT yarn displayed both semiconductive and metallic isotropic behavior with a resistance minimum, similar to the behavior of crystalline graphite. It was found that, at room temperature, the semiconducting contribution—most likely junctions between CNTs—accounted for 99.99% of the overall resistance. The resistance of forest grown CNT yarn and super acid solution spun CNT fiber decreased monotonically with temperature at a rate similar to amorphous carbon. The impedance of all three materials was also measured to 30 MHz. All three materials followed a series resistor inductor circuit, without any resistance decrease as others have found. Finally, the conductivity and specific conductivity of all three materials was compared to metallic benchmarks. While all three materials had a similar conductivity, the floating catalyst CNT yarn had a significantly higher specific conductivity.
# TABLE OF CONTENTS

## CHAPTER 1: INTRODUCTION AND BACKGROUND .............................................-1-

1.1 Thesis Introduction ........................................................................................---1-

1.2 Bulk CNT Materials........................................................................................-2-

1.2.1 Forest Growth CNT Yarn ..........................................................................-2-

1.2.2 Floating Catalyst CNT Yarn ......................................................................-5-

1.2.3 Super Acid Spun CNT Fiber ......................................................................-6-

1.3 CNT Conduction .............................................................................................-8-

1.3.1 Individual CNT Conduction ......................................................................-8-

1.3.2 Conduction Across CNT Junctions ..............................................................-11-

1.3.3 Bulk CNT Conduction ..............................................................................-15-

## CHAPTER 2: EXPERIMENTATION ................................................................-20-

2.1 Resistance Versus Temperature .....................................................................-20-

2.1.1 Contact Resistance ....................................................................................-20-

2.1.2 Room Temperature Resistivity ..................................................................-24-

2.1.3 Room Temperature Specific Conductivity .................................................-28-

2.1.4 Resistometry Set-Up ..................................................................................-30-

2.1.5 Resistometry Results and Discussion .........................................................-31-

2.2 Resistance Versus Frequency .......................................................................-39-

2.2.1 Frequency Dependence Background .........................................................-39-

2.2.2 Measurement Set-Up ..................................................................................-43-
LIST OF FIGURES

Figure 1 Forest grown CNT yarn being spun .............................................................-4-
Figure 2 Aerogel in floating catalyst CVD ...............................................................-7-
Figure 3 Super acid solution spinning process ......................................................-7-
Figure 4 Various CNT chiralities .............................................................................-9-
Figure 5 Experimentally determining ballistic length by dunking CNT in Hg ...........-11-
Figure 6 Diagram of junction conductance versus overlap ....................................-12-
Figure 7 Picture of crossed CNTs .............................................................................-15-
Figure 8 Resistance versus temperature for various disordered conductors ..........-18-
Figure 9 Annealed bulk CNT materials .................................................................-19-
Figure 10 Resistance versus length, floating catalyst CNT yarn .............................-22-
Figure 11 Resistance versus length, forest growth CNT yarn ..................................-22-
Figure 12 Resistance versus length, super acid solution spun ...............................-24-
Figure 13 SEM of CNT yarn diameters .................................................................-25-
Figure 14 Conductivity comparison of bulk CNT materials ...................................-27-
Figure 15 Conductivity comparison with carbon fiber and copper added ..............-27-
Figure 16 Specific conductivity comparison ..............................................................-29-
Figure 17 Specific conductivity comparison with aluminum .................................-30-
Figure 18 Resistance versus temperature, floating catalyst CNT yarn .................-32-
Figure 19 Resistance versus temperature fit ............................................................-32-
Figure 20 Resistance versus temperature, floating catalyst CNT cloth ..................-34-
Figure 21 Fit attempts for forest growth CNT yarn ...............................................-34-
Figure 22 Amorphous carbon comparison to forest growth CNT yarn ..................36-
Figure 23 Resistance versus temperature, solution spun CNT yarn: thick ..........36-
Figure 24 Resistance versus temperature, solution spun CNT yarn: thin ..........38-
Figure 25 Amorphous carbon comparison to solution spun CNT yarn ..........38-
Figure 26 Impedance versus frequency for CNT bundles ..........................40-
Figure 27 Fitting data to RC circuit .................................................................42-
Figure 28 Impedance versus frequency for CNT films ...............................42-
Figure 29 Impedance versus frequency for floating catalyst, past results ..........43-
Figure 30 LCR set up .......................................................................................44-
Figure 31 Nickel chrome Re[Z] versus frequency ........................................47-
Figure 32 Nickel chrome Im[Z] versus frequency ........................................48-
Figure 33 Floating catalyst CNT yarn Re[Z] versus frequency ....................49-
Figure 34 Floating catalyst CNT yarn Im[Z] versus frequency ....................50-
Figure 35 Forest growth CNT yarn Re[Z] versus frequency .........................51-
Figure 36 Forest growth CNT yarn Im[Z] versus frequency .........................52-
Figure 37 Solution spun CNT yarn Re[Z] versus frequency .........................54-
Figure 38 Solution spun CNT yarn Im[Z] versus frequency .........................55-
Figure 39 Network analyzer set up .................................................................55-
Figure 40 Floating catalyst CNT yarn Re[Z] versus frequency ....................56-
Figure 41 Floating catalyst CNT yarn Im[Z] versus frequency ....................56-
Figure 42 Forest growth CNT yarn Re[Z] versus frequency .........................57-
Figure 43 Forest growth CNT yarn Im[Z] versus frequency .........................58-
ACKNOWLEDGEMENTS

The author would like to acknowledge:

people at RZPG for their effort, team work, and vision pushing things forward,

Larry Christy for his help tackling all these issues together,

John Zentner for his expertise in high frequency impedance measurements,

Will Lanter and those at RZPE for helping build, run, and test their equipment,

David Anderson and others at the Materials Directorate for all the collaborating,
brainstorming, and hard work with the post treatment studies and characterization,

my thesis advisor, teacher, and mentor Dr. Kozlowski for all the help though the
everything.
CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Thesis Introduction

Bulk carbon nanotube (CNT) yarn, CNTs collectively spun together into a bulk textile, is an emerging, game changing technology-potentially competing with copper in niche electrical power transmission applications [1]. Individual CNTs may have high conductivity (several factors over copper) [2], high current carrying capacity ($10^9$ A cm$^{-2}$) [3], high thermal conductivity ($3500$ W m$^{-1}$K$^{-1}$) [4], large electron mean free path (65 µm) [5, 6, 7], and low density relative to conductive metals such as copper. With CNTs collected in a bulk ensemble, however, these merits greatly diminish with bulk resistivity to at least two orders of magnitude worse than copper. Possible reasons for this degradation include crystalline defects in the CNTs themselves and highly resistive junctions between the CNTs [8].

Determining the exact source of this degradation in bulk conductivity is the aim of this study. To accomplish this, resistance versus temperature and resistance versus frequency were measured across a variety of leading CNT bulk materials. It is important to remember that just because these materials are made from collected CNTs in general, processing methods and differences in CNT quality make for a very wide variety of mechanical and electrical properties. Resistometry, or measuring change in resistance versus a change in temperature, reveals the various possible conduction mechanisms within a CNT yarn [9]. As far as frequency dependence is concerned, several papers report significant drops in resistance beyond ten GHz, but this is with small collections of
Several producers of these bulk CNT materials, however, claim significant resistance drops in the MHz range [8]. Considering the source of the proposed resistance drop is the internal CNT geometry, verifying the producers’ results may also shed light on the conduction mechanisms.

1.2 Bulk CNT Materials

This study treated and evaluated three types of bulk CNT materials manufactured through different fabrication processes: 1) Solid state spinning from aligned CNT forests, 2) Solid state spinning from floating catalyst chemical vapor deposition (CVD), and 3) super acid solution spinning. All three techniques lend themselves to potential scale-up and commercialization. With both solid state spinning techniques, the CNTs grow orders of magnitude longer than other bulk production techniques and, all other factors being equal, longer CNT length implies a stronger, more conductive CNT yarn. Longer length CNTs, however, demand faster growth rates leading to decreased CNT crystallinity which impacts transport properties. Super acid solution spinning, on the other hand, is made from significantly smaller CNTs, but are nearly completely single wall CNTs (SWCNT) with high degrees of alignment along the fiber axis. [13].

1.2.1 Forest Growth CNT Yarn

Forest grown CNT yarn, one example of solid state spinning, mechanically pulls aligned CNTs off a substrate and twists them into a bulk CNT yarn—a process very similar to the ancient practice of spinning wool into yarn. The process starts with a substrate, such as a silicon wafer, coated with catalyst nanoparticles containing at least either iron, nickel, or cobalt. Under thermal CVD, a carbon gas, such as methane or
acetylene, is introduced to the substrate while it is heated to 600°C - 800°C. The catalytic metal nanoparticles decompose the carbon gas and carbon saturates into the metal nanoparticle. At the point of carbon oversaturation, carbon begins to emerge from the catalytic nanoparticle, ultimately resulting in the growth of the CNT. Nanoparticle size primarily determines CNT diameter. Optimization of the multitude of CVD growth parameters lead to long length (greater than one centimeter), vertically aligned CNT forests. Different catalyst compositions, water assisted growth, as well as aluminum oxide supports for layers below the catalyst are techniques employed for synthesizing better CNT forests [14].

Utilizing vertically aligned CNT forests, Jiang et al.[15] found as they plucked several aligned CNTs from its silicon substrate other adjacent CNTs followed. This effect stemmed from van der Walls forces keeping the CNTs together. Jiang explains that vertical, highly aligned CNTs enable van der Walls forces to line the CNTs together as they are pulled and assemble the yarn. The tip size of the spinning tool determines the thickness of the bulk CNT yarn because, the more CNTs initially picked, the thicker the yarn [15]. Others found that if the canopy of the aligned CNT forest twists together in a disorganized manner, it facilitates CNT yarn production because the CNTs mechanically lock together when pulled. Keeping the CNTs clean from amorphous carbon increases the van der Walls forces between them, also helping with CNT yarn production [14].
Figure 1. Aligned CNTs pulled from substrate take their then adjacent neighbors and form a CNT yarn--provided sufficient van der Walls interaction between CNTs exists. Starting from the left: graphical illustration of CNTs sticking to each other as they pull off the substrate, close up of aligned forest receding as CNT yarn forms, actual SEM images demonstrating the drawing process. On the bottom, a SEM close up of the full CNT yarn [15-18].

GeneralNano Inc. affiliated with the University of Cincinnati, graciously provided forest-grown CNT yarn for this study. The CNT yarn received was made from CNT forests 400 µm high with a CNT density $10^9$ CNTs/cm$^2$. Testing performed by the University of Cincinnati indicated double wall CNTs were formed with thermal
gravimetric analysis (TGA) showing less than 3% residual matter after burning. In the CNT yarn itself there were 15 twists per millimeter.

1.2.2 Floating Catalyst CNT Yarn

Floating catalyst CNT yarn, another form of solid state spinning, derives from a CNT aerogel mist produced by floating catalyst CVD. Typically, within the CVD chamber, an oxygen containing carbon gas, such as ethanol, serves as the carbon source, ferrocene as the source of iron catalyst, and thiophene as the growth promoter. Mixed together in a hydrogen carrier gas, the gases flow to the chamber’s hot zone, typically 1050°C - 1200°C. Here, the carbon gas decomposes and CNTs begin to grow around the iron catalyst similarly to the forest grown CNTs described above. Instead of growing vertically aligned on a substrate, however, the CNTs form into a hot, collective solid/gas colloid called an aerogel. The hydrogen gas flow carries this aerogel to a cooler section of the furnace where a mechanical roving arm sweeps through the mist and collects the CNTs into a bulk material, such as CNT yarn or sheet [19].

Like with all forms of CVD, a multitude of floating catalyst CVD parameters must be optimal to synthesize a high quality bulk CNT material. In particular, the carbon source should contain oxygen as a component. Researchers theorize that when this oxygen containing carbon gas decomposes, excess carbon reacts with the oxygen and forms carbon monoxide, rather than forming amorphous carbon that kills the catalyst. Also, increasing the flow rate of the hydrogen carrier gas tended to increase the preponderance of SWCNTs over multiwall CNTs. In addition, the faster the winding rate, the rate in which the mechanical arm sweeps through the aerogel, the higher then density
and alignment. If too fast, however, the material pulled from the aerogel begins to break [14].

1.2.3 Super Acid Spun CNT Fiber

CNTs, especially SWCNTs, clump together when placed into liquids due to strong van der Walls interactions. Hence, CNTs do not readily dissolve into solutions without functionalization, or chemically modifying the CNT surface. Functionalization, however, significantly alters the CNT properties, often for the worse. Super acids are the exception to this rule. Through protonization, CNTs electrostatically repel and overcome their mutual van der Walls attraction—allowing for the CNTs to dissolve as a solution. In these super acids, CNTs act as rigid rods and, with sufficient super acid concentration, become a fully liquid crystalline solution. To make a bulk CNT fiber, this solution extrudes through a mixture of water or less concentrated acid, protonization reverses and through flocculation, CNTs collect into a bulk fiber [14].

Researchers at Rice University applied this production technique with CNTs generated through High Pressure CO Conversion (HiPCO). This process generates predominantly short (around 10 nm), highly crystalline SWCNTs opposed to an ensemble of CNT types, such as multiwall and double walls, that other techniques tend to generate. Thus, bulk fibers produced by HiPCO, although much shorter, offer the possibility of very pure SWCNT compositions [14]. Rice University graciously provided super acid based solution spun bulk CNT fiber for this study.
Figure 2. On the left, the CNT aerogel appears as wispy black smoke in the heat zone. On the right, a diagram illustrating how the aerogel collects into a bulk CNT material [19].

Figure 3. Top picture group: A. Apparatus shown mixing and extruding CNT super acid solution. B. CNT fiber extruding from the device. C. Spooling the fiber after extrusion. Bottom picture group: A. Purified CNTs clumped together. B. Close up of the clump showing disordered tangled CNT ropes. C. CNT fiber after super acid solution spinning. D. Close up shows aligned CNT ropes. These images are courtesy of Pasquali’s group at Rice University [20].
1.3 CNT Conduction

An individual, single wall CNT (SWCNT) may be either metallic or semi-conducting. If metallic, they carry vast current with mean free paths that are orders of magnitude above other materials [21]. A collection of CNTs form electrical pathways where conductance between CNT junctions are, at best, a small fraction of a CNT’s intrinsic conductance, but is likely to be much worse. With an ensemble of CNTs, with thousands to trillions of CNTs, the CNT junction resistance limits overall conductance of the CNT yarn [9].

1.3.1 Individual CNT Conduction

Due to the cylindrical nature of SWCNTs, periodic boundary conditions bound the electron wave functions and, consequentially, these functions exist in quantized states dependent on the exact crystal structure. In particular, the CNT’s degree of crystalline twist, the chirality, dictates how it conducts electricity--either metallic in nature or semi-conducting. The chiral vector describes this crystalline twist, as well as every possible SWCNT geometry based off the graphene lattice. Refer to the left diagram in Figure 4 below. Unit vectors $a_1$ and $a_2$ form the graphene basis for the chiral vector. The slanted, parallel lines represent where the graphene lattice is cut and rolled into a cylinder to form the SWCNT. The chiral vector starts at a carbon atom on one side of the cut graphene plane and ends on the other side, with the carbon atom that would be in its position if the graphene lattice actually rolled into a SWCNT. Thus, the chiral vector relates to the SWCNT twist as well as to the SWCNT diameter [21].
Pure metallic CNTs possess a chiral vector \((m, n)\) such that \(m = n\). CNTs with a chiral vector such that \(m-n\) is a multiple of three semi-metals with a very small semiconducting band gap. At room temperatures, they transport electricity similarly to metallic CNTs. With these CNTs, the \(\pi\) orbitals of each carbon atom, perpendicular to the SWCNT surface, overlap. When \(m-n\) is not a multiple of three, then the SWCNT is semiconducting with a large band gap. As a result of this rule of three, all things being equal without special processing steps, when growing SWCNTs, one may expect one third will act metallic and the remaining two thirds semiconducting [21].

Theoretically, metallic SWCNTs have a resistance of 6.5 k\(\Omega\), independent of length, up to a point called the ballistic length. The 6.5 k\(\Omega\) is an intrinsic contact resistance called quantum conductance, or \(h/4e^2\) with \(h\) Planck’s constant and \(e\) the electron charge. Afterward this intrinsic contact resistance, electrons travel down the CNT ballistically, meaning phonons and other disturbances do not interfere with electron transport. As a consequence, the only resistance is the intrinsic contact resistance and overall resistance does not scale with length [5,21].

![Diagram of SWCNTs](image)

**Figure 4.** Left and middle diagrams illustrate a (5,3) SWCNT. Beginning on one side of the graphene cut, three steps in the \(a_2\) direction are taken and then five steps in the \(a_1\) direction. It ends on the carbon atom that would overlap with the starting carbon atom were the graphene plane actually rolled into the SWCNT. Diagrams on the right are three different SWCNTs showing different flavors of twist. The (12,0) and (6,6) have metallic behavior [21].
Poncharal et al. [7] demonstrated this ballistic effect by gingerly submerging outcroppings of multiwall CNTs into a bath of liquid mercury at room temperature while recording resistance versus submersion depth. These researchers found a conductance very near the conductance quantum that did not scale with submersion depth, up to 65 µm. This is an amazing length orders of magnitude greater than other materials typically no greater then tens of nanometers. Up to a point, however, the conductance jumps another multiple of the conductance quantum, indicating the entry of another multiwall CNT in parallel as the outcropping sinks lower. Poncharal makes the point that these multiwall CNTs were pristine and utilized as is, without any post treatment processes. This contrasts other measurement techniques that greatly alter the CNTs through post growth processes and result in less illustrious and diffusive conduction measurements [7].

As a consequence of ballistic conduction, metallic CNTs also carry vast amounts of current. Yao et al. [3] experimentally demonstrated SWCNTs with current densities greater than $10^9$ A/ cm$^2$. White and Todorov theoretically demonstrated that ballistic length scales linearly with CNT radius [5]. In light of this fact, larger radius CNTs, such as multiwall CNTs, may more efficaciously transport current in an ensemble as found in bulk CNT materials.
Figure 5. Multiwall CNTs grow through the arc generation process and are collected off the electrode as a large carbon outcropping. Multiwall CNTs protrude from this outcropping and then submerge into liquid mercury baths. The conductance is independent of submersion depth indicating ballistic transport. The conductance does change however as other CNTs plunge into the bath in parallel [7].

Beyond the ballistic length, the probability of an electron interacting with a phonon increases significantly and resistance does begin to increase with length. Purewall et al. [22] experimentally verified that, beyond the ballistic length, metallic CNTs follow Eq. (1) below.

\[
\text{resistance (length)} = h(4e^2)^{-1}\left(1 + \frac{\text{length}}{L_m}\right) \tag{1}
\]

where \( h \) is Planck’s constant, \( e \) electron charge, and \( L_m \) the ballistic length. Related experiments by Li et al. [2] confirm this finding with ultra long SWCNTs more than four millimeters long. Their results agree with past work that metallic CNTs resistance scales with length at approximately six kΩ per micron.

1.3.2 Conduction Across CNT Junctions

On the scale of individual SWCNTs, researchers theoretically calculated and experimentally measured junction conductivity between two SWCNTs. Buldum et al.
[23] numerically modeled SWCNT junction conductivity as a function of SWCNT chirality and relative orientation. The model showed junction conductivity is comparable to pure SWCNT conductivity when two metallic SWCNTs are parallel aligned and in atomic scale registry—that is, the atomic lattices between both SWCNTs perfectly align. Not surprisingly, as the overlap distance between SWCNT increases, the junction conduction increases, but, as shown below, this increase is quasi-periodic as the SWCNT lattices slide back into alignment.

![Diagram](image)

Figure 6. Buldum et al.[23] calculates theoretical SWCNT junction conductivity by a π-orbital tight binding Hamiltonian, with electron-electron interaction excluded. In (a), a parallel orientation yields the highest possible conductivity junction that increases quasi-periodically with overlap distance $l$, shown in (b). $G$ is conductance quantum. Shown in (c), electron transmission probability versus electron energy.

Figure 6 shows conductivity between two armchair CNTs with mutual chiralities of (10,10) and, depending on the lattice alignment, a conductivity 20-40% the conductance quantum, or the theoretical conductance of one metallic SWCNT. The probably of two SWCNTs sharing the same chirality, as well as perfectly aligned lattices adjacent to each other, is low. These appreciable fractions of quantum conductance are, perhaps, an upper bound for the conductivity between untreated CNTs. Further modeling
by Buldum [23], and earlier by Fuhrer [24], however demonstrates that SWCNT junction conductivity significantly improves when pressure squeezes them together, especially for in-registry SWCNTs lattices. Fuhrer provides a calculated example. Consider two perpendicular armchair SWCNTs, both with chiralities (5,5). Simulating substrate interaction, 15 nN is numerically applied to the SWCNT junction and the separation squeezes from the graphite van der Walls distance of .34 nm to .25 nm. Electron transmission/tunneling probability jumps from 2E-4 to 4E-2, all in good agreement with experiment. The modeled SWCNT diameters were approximately 1.4 nm [23,24]. With the given substrate interaction force of 15 nN, this corresponds to an 8 GPa pressure.

Further modeling by Buldum illustrates that junction conductivity between two metallic, crossed SWCNTs varies by a factor of 800 as angle sweeps between 0 to 180 degrees. Again, the highest conductivity angles were those that resulted in in-registry lattices. Surprisingly, their model shows that junction conductivity decreases as the SWCNT diameters increase. Buldum explains that, although larger contact areas go with larger diameter SWCNTs, the larger diameters reduce the relative weight of the electron wave functions around the contact area and the probability of electron transmission decreases [23].

In verification of these theoretical models, Fuhrer explored SWCNT junction conductivity experimentally. His team performed a four probe resistance measurement on two SWCNTs crossing. If resistance of an individual SWCNT depended on gate voltage, it indicated that particular individual SWCNT was semiconducting. If the resistance was independent of gate voltage, the SWCNT was metallic. Thus, possible permeations of SWCNT junctions were metallic/metallic, semiconducting/semiconducting, and
semiconducting/metallic. Four probe resistance measurements revealed that the metallic/metallic junctions were approximately 8% the conductivity of a metallic SWCNT, and semiconducting/semiconducting was around 4%. Semiconducting/metallic junctions, however, formed a Schottky barrier with conductivities two orders of magnitude lower [24].

Note, however, that these experimental conductivities apply for nearly perpendicular junctions with, as discussed above, very significant substrate interaction. The conductivity of a CNT ensemble, such as a bulk CNT material, is logically likely to be dominated by larger, more conductive junctions between CNTs that overlap across a continuum, not cross at a point. Also, the pressure, and resultant conductivity enhancement, found with the substrate interaction is most likely absent. Drawing from these experimental results however, it can be inferred that conduction within a CNT ensemble happens between metallic/metallic or semiconducting/semiconducting junctions, and not with semiconducting/metallic junctions. Thus, electrons traveling down a bulk CNT material stay within a strictly metallic sequence of CNTs or strictly a semiconducting sequence, with no hopping between type. Considering that metallic CNTs are significantly more conductive then semiconducting CNTs, at least without post treatment, it can be inferred that semiconducting CNTs, as is, play little role in the conduction of bulk CNT materials.
Figure 7. (a) AFM image of Fuhrer’s crossed SWCNT junctions. (b) Conductance for metallic/metallic, semiconducting/semiconducting, and semiconducting/metallic. (c) Modeling shows substrate interaction applies significant pressure pushing SWCNTs closer together and deforming their structure [23].

1.3.3 Bulk CNT Conduction

On the bulk scale, literature reports several conduction mechanisms competing within bulk CNT materials. Fischer et al. [9] explored these mechanisms by varying the material’s temperature and measuring their resistance change. First, his team produced SWCNTs from the laser ablation CNT growth process. X-Ray Diffraction and Raman Spectroscopy confirmed that these SWCNTs were metallic, armchairs with chirality (10, 10) and diameter 1.38 nm. Due to van der Walls binding, the SWCNTs assemble into tightly packed SWCNT bundles, hundreds in number and tens of microns long with spacing between SWCNTs .32 nm. A copper collection plate gathered the bundles as they fell and eventually formed thick carbon mats. To remove fullerenes and left over catalyst, Fischer’s team heat treated the samples at 1000°C, 30 minutes in an inert environment. Fischer measured the resistivity versus temperature on these mats as well as the individual SWCT bundles themselves [9].
In general, the complied mats’ resistivities measured approximately 50 times greater than the individual, smaller bundles. Above a certain temperature, both the bundles and mats behaved similarly with a metallic temperature dependence of resistivity, \( \frac{d\rho}{dT} > 0 \). At some cold cross over temperature \( T^* \), however, which varied from sample to sample, both the mats and the bundles demonstrated semi-conductive characteristics with \( \frac{d\rho}{dT} < 0 \). For mats with low yields of SWCNT, they demonstrated \( \frac{d\rho}{dT} < 0 \) all the way to 307°C, the measurement limit of the experiment. Fischer explains this semi-conducting behavior over the entire temperature range resembles previous, similar studies of multiwall CNTs where defects are more frequent and play a greater role on the conduction process. Supporting the concept that SWCNT junctions play a significant role in bulk CNT materials, Fischer pressed down on the mats and measured a significant change in the bulk resistivity. By a slight pressure of 4 kg/cm\(^2\), the resistivity decreased by a factor of 3 [9].

Kaiser et al. [25] demonstrates that Fischer’s measurements above follow the behavior of well known conductive polymers, which follow an established heterogeneous conduction model. In this model, conductive regions are separated by barriers to conduction. In this case, these barriers may be SWCNT vacancy defects, interconnections between SWCNTs, and tangled regions of the bundles. As temperature increases, the metallic SWCNTs become more resistive and the barriers, with semiconducting properties, become less resistive. This leads to a minimum of the resistance versus temperature curve, \( T^* \). The resistivity versus temperature of conductive polymers are described the following equation.
\[
\rho(T) = \rho_m e^{-\frac{T_m}{T}} + \rho_t e^{\frac{T_c}{T_s}}
\]  
(Eq 2)

where \(\rho_m, \rho_t, T_m, T_c,\) and \(T_s\) are constants to be fit to the data. The first term is the highly anisotropic metallic term where phonons of energy \(kT_m\), traveling along the length of the SWCNT, backscatter charge carriers--appropriate for one dimensional conductors such as SWCNTs. Kaiser’s finds that this metallic resistance contribution, or the resistance of the SWCNTs themselves, account for only 5% of the overall total room temperature resistance. The second term in Equation 2 corresponds to electron tunneling/hopping between insulating, thin barriers. His fittings for \(T_c\) and \(T_s\) are comparable to those of the conductive polymers equation 2 was originally intended for. Some of the analyzed samples, however, fit better with a standard linear metallic resistivity term. Equation 2 becomes

\[
\rho(T) = A T + \rho_t e^{\frac{T_c}{T_s}}
\]  
(Eq 3)

with \(A\) the metallic linear parameter. Even in this case, Kaiser again explains that the metallic contribution, at room temperature, is a small fraction of the bulk resistance--most of the resistance coming from the semiconducting junctions. Figure 8 below shows Kaiser’s fittings to Fischer’s data, as well as the data fittings of the original conductive polymers Equation 2 was originally meant for [25].
Figure 8. Relative resistance versus temperature of several disordered conductive materials: Microscopic CNT bundles, macroscopic CNT mats, and conductive polymers. The fits to this data illustrate the metallic and semiconducting behavior [25].

Kulesza et al.[26] performed a similar resistivity experiment, but, instead of Fischer’s SWCNT mats, Kulesza instead measured another bulk CNT material, Bucky paper, generated by the arc discharge CNT process. Carbonized electrodes, impregnated with catalyst, arced and produced soot in an inert environment. This soot, a collection of CNTs, fullerenes, and amorphous carbon, was collected and treated with an aqueous solution of 3 M nitric acid, 110°C, for 20 hours. The solution doped the SWCNTs and eliminated impurities such as the remaining catalyst and amorphous carbon. The soot was filtered out and rinsed with water. With this cleansing process repeating several times, eventually this soot was allowed to dry and it began clumping together forming the bulk CNT material Bucky paper. Raman spectra showed that this Bucky paper was composed primarily of semiconducting SWCNTs. In contrast to Fischer’s metallic SWCNTs from above, Kulesza explains the semiconducting preponderance originates from defects introduced by the nitric solution [26].
Figure 9. On the left, nitric acid doped Bucky paper--conductance changes dramatically with temperature, but behavior is monoatomic unlike the CNT mats above. In the middle, TEM images of the Bucky paper and, on the right, Bucky paper after annealing. The annealed Bucky paper, with the shown increased alignment, is about twenty times more conductive then before [26].

Figure 9 above shows the Bucky paper’s conductance versus temperature. Unlike Fischer’s metallic SWCNTs, Kulesza conductance monotonically increases with temperature. There are two distinct temperature regions, however, that point to two different conduction mechanisms. Kulesza found one was metallic and the other semiconducting, but unlike Fischer, Kulesza found these terms fit when added in parallel and not in series. Equation 4 best fit Kulesza’s data

$$\frac{1}{R(T)} = \frac{A}{T} + Be^{-\frac{C}{T}}$$  

(Eq 4)

where A, B, and C are parameters to be fit to the data. Kulesza later heat treated his prepared samples at 627° C in vacuum. They found that the parallel model from above still fit the data, but resistance varied less with temperature and the room temperature resistance improved by a factor of 20. Interestingly, also shown in Figure 9, the annealing process tended to align the CNTs within the Bucky paper—which, in addition to healing atomic defects and cleaning impurities, would result in the higher conductivity they found [26].
CHAPTER 2

EXPERIMENTATION

2.1 Resistance versus Temperature

Resistance versus temperature of all three types of bulk CNT materials was measured. To accomplish this, contact resistance must be considered. In considering contact resistance, this will be a natural place to consider overall resistivity and how it compares with metallic benchmarks. Results and discussion of the measurements will follow.

2.1.1 Contact Resistance

The contact resistance (the resistance between the test lead’s metallic interface, in most cases silver paint, and the CNTs themselves) has to be determined prior to resistometry measurements of bulk CNT materials. Although this contact resistance plays an important role, contact resistance is not an inherent material property by itself and will complicate fitting conduction models to the measured data. Thus, an effort was made to take this contact resistance into account.

The most common way to measure contact resistance is the four point probe technique where two isolated electrical probes connect to each end of the material, making a total of four probes. The two most outer probes inject a known current through the sample. The two most inner probes, the sensing probes, measure the voltage drop via highly resistive lines. The fact that these inner sensing lines are highly resistive ensures that most of the injected current runs through the sample, guaranteeing that a voltage
drop by just the material itself is measured. This minimizes the contribution from contact resistance.

Unfortunately, a robust four probe technique was not available for the resistometry and impedance measurements. Also, due to the inherent nature of the CNT yarn processing, the consistency of the material has been raised from one length segment to another—such as a variable diameter or kinks in the CNT yarn. As a result, we measured resistance per unit length to back out contact resistance and gauge variability of the material.

The contact resistance by measuring the resistance of the material versus its length was determined. After plotting the resistance versus length data, the vertical axis intercept, or the remaining resistance when length is zero, is the contact resistance. For various lengths of floating catalyst CNT yarn and forest grown CNT yarn, we silver painted cleaned copper leads to their CNT yarns’ ends and allowed them to dry overnight. Using a multimeter, the resistance in ambient room conditions was measured. As shown in Figure 10, for the floating catalyst CNT yarn, resistance versus length was plotted.
Figure 10. Floating catalyst CNT yarn, resistance versus length. As shown with the straight line, the material’s electrical properties are relatively consistent as we measured up to 22 cm CNT yarn segments. The contact resistance, however, is large at 147 Ω.

Figure 11. Forest grown CNT yarn, resistance as a function of length. For this material too, the electrical properties are relatively consistent up to 23 cm. Contact resistance is 62 Ω.
Fitting the data to a line, we find that the resistance at zero length, the contact resistance with silver paint, is 147 Ohms. For the resistometry measurements, the samples typically were five centimeters long. Thus, contact resistance, at least in ambient conditions, accounted for half the overall resistance of the floating catalyst CNT yarn—a major measurement problem that is addressed later.

For the forest grown CNT yarn, at the time less material was available, so we considered only three different lengths as shown in Figure 12. For the forest grown CNT yarn, contact resistance between silver paint was 62 Ohms. For the five centimeter pieces used in the resistometry, this contact resistance accounted for 5% the overall resistance in ambient conditions. Note, the resistance per unit length is approximately ten times greater than the floating catalyst CNT yarn. Partly this is due to the fact the average diameter of the floating catalyst CNT yarn is twice that of the forest grown CNT yarn.

For the super acid solution spun CNT fiber, received late in the study, we measured the contact resistance with copper leads mechanically pressed down into the ends of the material, without any intermediary such as the silver paint. As shown in Figure 12, the contact resistance was 75 Ohms for direct copper contact.

In addition to showing the contact resistance, the plots above show that resistances scales nearly linearly with length for all three materials. This implies the materials are relatively consistent in diameter and resistivity across the length of the bulk material.
Figure 12. Super acid solution spun CNT fiber, resistance as a function of length. This material is the least consistent out of the bunch, but resistance generally scales linearly with length. Contact resistance is 72 Ω.

### 2.1.2 Room Temperature Resistivity

From above, contact resistance and resistance per unit length were determined. If a value for the CNT yarn’s diameter could be found, we might also calculate resistivity and compare the three materials. Resistivity comparisons for such porous, variable textiles are not exactly a fair metric. First, being a textile, pulling on the CNT yarn dramatically reduces the diameter and hence the resistivity calculation. To complicate matters, pulling on the fiber also places radial inward pressure on the CNTs—potentially improving contact connections and changing the actual resistances measured. Thus, for resistivity, relaxed CNT yarns not under tension were only considered.

Furthermore, another problem with the resistivity metric, is that it does not account for density. Two CNT yarns of equal diameter may own vastly different resistances solely based on the fact that one simply has more conduction channels, is less porous, and weighs significantly more. The resistivity metric never takes the greater weight into account. Specific conductivity is another metric, introduced later, that
compliments comparisons between materials. Finally, another problem with the resistivity metric is that, due to processing conditions, the diameter of the yarn varies as one travels down its length. After inspection under scanning electron microscope (SEM), however, we found this variability not as great as we expected, but it leads to the most significant source of error in the resistivity calculation.

The SEM captured the yarn morphology and, by scanning several CNT yarn sections, collected enough data to calculate an average diameter. Snippets of CNT yarn were placed carefully onto SEM stubs with silver paint and took care to minimize lateral strain that distort the CNT yarn’s diameter. Under SEM, we calculated an average CNT yarn diameter by looking at four different 50 µm sections of each CNT yarn sample. In roughly two micron intervals, the diameter using a calibrated scale bar was measured. From this, we could calculate an average diameter and standard deviation.

Figure 13. Typical SEM images of CNT yarns, the one of the left is forest grown CNT yarn and the one on the right is floating catalyst CNT yarn. Even under high resolution, individual CNTs could not be resolved. This twist in the CNT yarn, however, is apparent. In addition, outcroppings of CNT bundles randomly jet from the main fiber.
Diameter

Floating catalyst CNT yarn: 56.46 ± 4.0 µm
Forest grown CNT yarn: 28.45 ± 0.79 µm
Super acid solution spun CNT yarn (thin): 42.30 ± 2.1 µm
Super acid solution spun CNT yarn (thick): 96.04 ± 0.94 µm

Resistivity

Floating catalyst CNT yarn: 6.4 ± 0.9 µΩ m
Forest grown CNT yarn: 14.3 ± 0.8 µΩ m
Super acid solution spun CNT yarn (thin): 6.88 ± 0.03 µΩ m
Super acid solution spun CNT yarn (thick): 138 ± 0.1 µΩ m

Now that the average diameters are known, the cross-sectional area may be calculated, followed by the resistivity.

For comparison, Figure 14 shows the conductivity of the CNT yarns. At this point, floating catalyst CNT yarn has the highest conductivity by a slight margin, followed by super acid solution spun CNT yarn, and then by forest grown CNT yarn. On a log plot, Figure 14 also shows the conductivity of the most conductive carbon fibers, graphitized at 3000 C—before and after Graphite Intercalation Compound (GIC) Treatment. In this case the GIC was arsenic (V) fluoride, and after treatment yielded some of the most conductive carbon compounds known—even more conductive than copper, also shown [30]. Despite the assumed greater crystallinity of the CNT yarns, their conductivity is significantly less than even the graphitized carbon fiber before GIC treatment.
Figure 14. Thin super spun CNT fiber has the highest conductivity, followed by floating catalyst CNT yarn, and then forest grown CNT yarn.

Figure 15. All CNT yarn types, however, have a long way to go to compete with graphitized vapor grown carbon fiber. Specially treated with Graphitic Intercalation Compounds, the carbon fibers even beat copper.
2.1.3 Room Temperature Specific Conductivity

As discussed above, the specific conductivity is a metric that takes density into account. We only need to measure resistance, length, and weight without bothering to gauge a variable diameter. With this, we take resistance per length and multiply it by a linear density. The inverse of this product is conductivity per density, or the specific conductivity.

\[
\left( \frac{\text{resistance}}{\text{length}} \cdot \frac{\text{mass}}{\text{length}} \right)^{-1} = \left( \frac{\rho}{\text{Area}} \cdot \sigma \cdot \frac{\text{Area}}{\text{length}} \right)^{-1} = (\rho \sigma)^{-1} = \frac{\text{conductivity}}{\text{density}}
\]

(Eq 5)

Thus, in order to calculate specific conductivity, we needed to determine the linear density. Professionals in the textile industry gauge linear density, or Tex, most often in the units of grams per kilometer. For a given length, we weighed the material with a microbalance to determine Tex. We also measured Tex directly by a vibroscope. Both linear density measurement techniques agreed nicely. Since we had the weight and the full dimensions, we could also calculate a standard, volume density. The density results are shown on the next page.

The forest grown CNT yarn has twice the density of the floating catalyst CNT yarn. The forest grown CNT yarn, however, has half the linear density because of its smaller yarn diameter. Now that we determined Tex, we could calculate specific conductivity. Figure 16 shows the results.
Density

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Linear Density--from length and mass (Tex or g/km)</th>
<th>Linear Density--from vibroscope (Tex or g/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floating catalyst CNT yarn--untreated</td>
<td>.51</td>
<td>1.27</td>
<td>--</td>
</tr>
<tr>
<td>Forest grown CNT yarn--untreated</td>
<td>.95</td>
<td>.6</td>
<td>.64</td>
</tr>
<tr>
<td>Super acid solution spun CNT fiber (thick)</td>
<td>1.12</td>
<td>6.7</td>
<td>--</td>
</tr>
</tbody>
</table>

Specific Conductivity

<table>
<thead>
<tr>
<th></th>
<th>Specific Conductivity (S m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floating catalyst:</td>
<td>305.5</td>
</tr>
<tr>
<td>Forest grown:</td>
<td>73.4</td>
</tr>
<tr>
<td>Super acid solution spun (thick):</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Figure 16. As far as conductivity per density, floating catalyst CNT yarn beats forest grown CNT yarn by several factors.
Figure 17. A good benchmark for conductivity per unit density is aluminum. Not only is aluminum very conductive and very light, it is also relatively inexpensive. With this metric, the CNT yarns have less of a margin to catch up to.

### 2.1.4 Resistometry Set-Up

We sanded and cleaned copper leads, approximately one centimeter in width, with isopropanol and acetone. We laid the CNT yarn across the leads and faceted them with silver paint, then allowed to dry overnight. We placed the CNT yarn sample atop a heater all within a vacuum chamber. From outside the chamber, we manipulated two internal electrical probes to make electrical contact with the CNT yarn copper leads. With these probes in place, a 4284A Agilent LCR meter measured the resistance at 20 Hz—which for our purposes is indistinguishable from DC. A Labview program automated the heater temperature control and collected LCR meter output.
Before turning on the heater, however, the chamber pumps down to at least a microTorr and often pumps down to tenths of microTorr. Once the pumps establish good vacuum, the sample bakes for one hour at 100°C and again at 200°C. These bakes cure the silver paint and outgas oxygen from the CNT yarn, which becomes destructive at higher temperatures. In increments of 100 degrees, the sample sits for thirty minutes before the LCR meter measures the resistance. This pause ensures thermal equilibrium between the sample and the heater’s thermocouple. Usually the sample underwent four temperature sweeps to ensure a consistent trend after outgassing. At first, these temperature sweeps went all the way to 900°C, but after one heater gave out, we limited the sweeps to 700°C.

2.1.5 Resistometry Results and Discussion

Figure 18 on the next page shows the resistance versus temperature behavior of floating catalyst CNT yarn. During the first temperature ramp to 900°C, the resistance significantly increases with temperature. This initial behavior is representative of all three CNT yarn types tested. Kozlowski reported in [32] that the outgassing of absorbed oxygen, which dopes the CNT yarn, causes this resistivity increase. In the case here, as well as the other CNT materials, after the first temperature ramp, all subsequent ramps follow a definite trend repeated with every other sweep. The actual repeated trend itself depended on the type of CNT yarn tested.

Figure 19 below magnifies the second run of Figure 18 above. Note this figure shows a minima around 500°C. As shown with Fischer’s mats, this behavior is
characteristic with bulk CNT materials depending on metallic and semiconducting mechanisms to the overall conductivity.

![Graph showing temperature vs. resistance for different ramps](image)

Figure 18. Floating catalyst CNT yarn, resistance as a function of temperature in vacuum. The first temperature sweep results in outgassing which increases the resistance. After outgassing however, the CNT yarn develops a constant trend that shows semiconducting/metallic behavior.

![Graph magnifying the second sweep](image)

Figure 19. The second sweep magnified of Figure 18 above. The red is the fitted line.

A problem with this data, as mentioned above was that contact resistance accounts for half the overall sample resistance—at least in ambient conditions. With the thermal baking, however, the silver paint cures and contact resistance should decrease,
improving the situation. Also, the resistance of the CNT yarn increases 75\% due to oxygen out gassing, lessening the contribution from contact resistance. Fitting the data to the conduction models mentioned in the background, for the floating catalyst CNT yarn, we consider two data sets, one as measured and the other with ambient condition contact resistance subtracted. The actual contact resistance, possibly a function of temperature, most likely lies somewhere between these extremes. Equation 6 below shows the fit with the data as is, with contact resistance and all. The fit is also shown as the red line above on Figure 19.

\[ \rho(T) = 1274 e^{-\frac{4511}{T}} + 166 e^{\frac{2768}{T+3429}} \]  

(Eq 6)

As with Fischer’s material, the data below, which does not subtract contact resistance, fits nicely to Equation 6 and supports highly anisotropic conduction along the length of the CNTs. Subtracting out the ambient condition contact resistance drops the semi conducting portion of Equation 6 above by a factor of three, but otherwise does not significantly alter the fit. In either fit, the ratio of semiconducting resistance to total resistance at room temperature yields 99.99\%. Thus, at room temperature, almost all resistance comes from junctions between CNTs. In comparison, Fischer’s CNT mats, which composed primarily of metallic CNTs, the room temperature semiconducting contribution was 95\%. These results and the past work mentioned suggest the first objective in improving CNT yarn conductivity is improving junction conductance, as opposed, say, to making the CNTs more metallic [9].

This metallic versus semiconducting behavior is also evident in other floating catalyst CNT materials. Obtained from Cambridge, Figure 20 below shows the
temperature dependence of floating catalyst CNT cloth—which has a significantly larger cross section than the CNT yarn materials and has a much lower resistance than the yarn equivalent. The minimum, however, happens around 277° C, pointing to a fundamentally greater metallic contribution than the floating catalyst CNT yarn above.

Figure 20. Floating catalyst CNT cloth, also showing semiconducting/metallic behavior.

Figure 21. Forest grown CNT yarn, conductance versus temperature. The red line shows a fit to the parallel conduction model, which worked nicely for other researchers. Here, the fit seems off.
We found that the ambient condition contact resistance was a third of an Ohm, so it should not significantly affect fitting. The fitted equation is below.

\[
\rho(T) = 107.5e^{-\frac{3769.7}{T}} + 17.5 e^{\frac{355.9}{T+1389.4}} \tag{Eq 7}
\]

Again, at room temperature, the resistances between CNTs account for 99.99% the overall resistance. Collier et al.[27] and others found similar minima behavior with pure graphite. Collier explains that with graphite, the higher the temperature and long lasting the annealing process, the more conductive the material and greater the minimum shifts to the left.

Forest grown CNT yarn yielded an entirely different behavior as shown in Figure 22. Note that the contact resistance contribution, at least at ambient conditions, was 5%. Here, in the second temperature sweep, we take the inverse of resistance, conductance, and see the trend is monoatomic, indicating that, without the minima behavior, a different conduction mechanism is at play. When looking at Bucky paper, Kulesza et al.[26] witnessed similar results. Their data fit well to a parallel conduction model that considers the metallic regions and the barriers to conduction to be in parallel– as opposed to in series as with the floating catalyst CNT yarn. The barrier term, however, is slightly modified to reflect thermally activated exponential decay over actual electron tunneling.

The fit with the forest grown CNT yarn however, as shown above, was not as close as Kulesza. In addition, with Kulesza’s material, the resistance changed over two orders of magnitude with temperature [26]. The temperature dependence in this situation is significantly more benign. Interestingly, as shown in Figure 22 below, the relative
change of resistance with temperature is very similar to the behavior of amorphous carbon (in this case, 80% petroleum coke and 20% lamp-black) [27]. Their slopes differ only by a factor of two. Thus, with untreated forest grown CNT yarn, it seems that any metallic contribution is dominated by semiconducting behavior.

Figure 22. Untreated forest growth CNT yarn follows the behavior of amorphous carbon as depicted by the black line [27].

Figure 23. Like the other materials, the thick version of the super acid solution spun CNT fiber reaches a consistent trend after the first sweep.
Super acid solution spun CNT fiber yields similar results as the forest grown CNT yarn--that is, the behavior resembles amorphous carbon as opposed to the crystalline graphite. Figure 24 on the next page below shows all four different temperature sweeps, with the first sweep indicative of typical out gassing.

This particular sample above was with what we termed thick fiber, which possesses a significantly larger diameter then the thin fiber. Due to the solution spun manufacturing processes, the thinner fiber has greater CNT alignment and greater conductivity.

Even with multiple temperature sweeps, this thin fiber above never established a consistent trend. Note that the resistance jumped again after the second sweep, near where CNTs would burn. We, at first, suspected residual atomic oxygen oxidizing the CNTs. The vacuum, however, was a microTorr or better. Just for this super acid solution spun CNT fiber, other researchers discovered significant resistance increases after high temperature annealing. They attributed this increase to loss of absorbed super acid that dopes the CNT fiber. Quite possibly, the progressive loss of acid dopant is what we are seeing here. Figure 24 below shows the second temperature sweeps of both the thick and thin fiber, superimposed over amorphous carbon results.

In summary, the floating catalyst CNT yarn behaves like graphite and has a resistance minimum. Fits to this data suggest anisotropic one dimensional conduction and that junctions between CNTs account for almost all the resistance in the material. Forest grown CNT yarn and super acid solution spun fiber behave like amorphous carbon with no metallic behavior observed.
Figure 24. The thin version of the super acid solution spun CNT yarn never really reaches a consistent trend. Possibly, the resistance changes after each temperature sweep due to left over super acid leaving the fiber at high temperatures.

Figure 25. Like the forest grown CNT yarn, the super acid solution spun CNT fiber acts like amorphous carbon as shown with the black line [27].
2.2 Resistance Versus Frequency

Measuring the impedance of a fine wire, especially one that allows for the possibility of interesting AC effects, is a deceptively tricky undertaking. There are reports of resistance drops at MHz frequencies due to capacitive coupling between CNTs in the bulk material [8]. We will investigate this claim.

2.2.1 Frequency Dependence Background

Impedance, the AC generalization of resistance, is the complex ratio between voltage and current in an ohmic material. The real part of impedance is resistance, which dissipates energy via Joule heating according to the formula, power

\[ \text{heat} = \text{current}^2 \times \text{resistance}. \]

In circuits without reactive elements, changing current immediately changes the voltage and vice-versa. In this non-reactive situation, impedance is resistance without any complex component. When reactive elements come into play, however, such as inductors and capacitors, the energy contained in these reactive element’s static fields may not change instantaneously. Consequentially, voltage and current lag each other in the overall circuit. Impedance expresses this lag, or phase shift, as a complex number [28].

It has been speculated that CNTs should have interesting impedance effects at high frequency [8]. In an effort to measure SWCNT impedance, Zhao et al.[12] produced SWCNT through the arc discharge process. His team first purified the produced SWCNT with standardized cleansing processes and then deposited them on a SiO₂ capped silicon wafer. Using a Focused Ion Beam, they fabricated four tungsten probes onto a selected SWCNT rope—a collection of several SWCNTs that clump together due to van der
Walls forces. Scanning Electron Microscope and Atomic Force Microscope measurements were used to ensure SWCNT rope uniformity and lack of contamination, such as left over catalyst.

Using an impedance analyzer, the impedance up to 8 MHz was measured and discovered that the CNT rope impedance follows a parallel resistor capacitor circuit. As shown in Figure 26 below, the real part of impedance, resistance, drops off with frequency. The reactance first goes up and then down again. Zhao explains this behavior with a negative capacitance and electron relaxation mechanisms within the CNTs. They conducted this experiment, however, with a microscopic amount of CNT material demonstrated to be semiconducting. The conduction mechanisms with bulk CNT material, where metallic CNTs dominate the conduction mechanisms, will likely behave differently [12].

![Impedance measurement](image.png)

Figure 26. For a small collection of SWCNTs called CNT ropes, the resistance drops significantly within the MHz range [12].

Tselev et al.[12] also measured the impedance of bundles of CNTs. First, Tselev functionalized CVD grown CNTs with an oxidation agent, such as nitric acid, which allowed the CNTs to dissolve in water. Next, he submerged an electrode in the solution and applied an AC electric field. With this technique, called AC field dielectrophoresis,
the CNTs in solution align with the gradient of the electric field from the electrode. Gingerly pulling out the submerged electrode tip from the solution, surface tension clumps the aligned CNTs together. The bundles analyzed were typically a micron long, with widths 100-180 nm in diameter. After post processing and substrate preparation, Tselev measured the bundle’s impedance from 10 MHz to 65 GHz with a network analyzer [10].

As shown in Figure 27 on the next page, the impedance spectrum fits a parallel capacitor resistor model, in series with a resistor and inductor. The parallel capacitor resistor represents the contact resistance and capacitance between the CNTs and the electrodes. At sufficiently high frequency, the current begins to short between this contact capacitance, circumventing the contact resistance, and the overall bundle resistance drops. Tselev also found that, considering the data fits the model, the individual model components, and hence the CNTs themselves, are frequency independent. The drop in resistance, however, is due to the high frequency bypass of the contact resistance at the electrodes. Potentially, other capacitive effects may exist in larger bulk materials [10]. Xu et al.[11] explored the conductivity of bulk five centimeter diameter SWCNT films using a network analyzer and a carbine reflection technique, which physically does not touch the sample. Xu explains that, in these bulk materials with percolating CNT networks, CNT junctions dominate the overall resistance. As shown in Figure 27 below, Xu found that the conductivity increases after 100 MHz, and dramatically increases after 2 GHz. Xu explained that the AC conductivity follows a disordered material power law, with conductivity proportional to $\omega^s$ with $\omega$ angular frequency and $s$ a parameter less than one. In this model, electrons hop from one conductive region to another and are separated by
thin barriers to conduction. In the cases of Xu’s SWCNT films, these regions are junctions between CNTs.

Figure 27. Tselev also performed similar experiments with CNT bundles and found the resistance drops with frequency, but this time in the GHz range. He also found the individual modeled components, such as the resistor representing actual CNT resistance, is frequency independent [10].

Figure 28. Measuring transparent CNT film, a bulk CNT material, Xu also finds the conductivity changes significantly only in the GHz range [11].

NanoComp Inc. the company that provided the floating catalyst CNT yarn, measured the impedance of the bulk CNT yarn using a function generator and oscilloscope. Unlike Xu’s thin film of CNTs above, this is a dense three dimensional ensemble of CNTs [11]. As shown in Figure 29 below, for a variety of post treated floating catalyst CNT yarns, they found that the resistance begins to roll around 100 kHz.
They too cited the capacitive coupling between CNTs as the source of this resistance drop [8].

![Figure 29](image)

Figure 29. For floating catalyst CNT yarns, there are reports of very significant resistance drops by 1 MHz. Here, several differently treated floating catalyst CNT yarns are shown in contrast to pure metallic wires of comparable diameter [8].

### 2.2.2 Measurement Set-Up

As discussed in the background, we expect the bulk CNT yarn’s resistance will drop due to capacitive coupling between its individual CNTs. Finding this resistance drop and the frequency range where it starts is a major objective of this study. Most applicable papers cite resistance drops with small amounts of CNT material in the GHz frequency range. The companies that manufacture the solid state spun CNT yarns, however, report a significant resistance drop in the tens of MHz frequency range.

Primarily, impedance using LCR meters was measured. An LCR meter applies a voltage across two terminals, at a particular frequency, and measures the resultant current amplitude and phase shift. Figure 30 below shows the Agilent 4284A (measuring impedance from 20Hz-1MHz) and 4285A (measuring impedance from 75kHz-30MHz).
LCR meters we used. Thus, we explored a frequency range up to 30 MHz with an overlap between 75 kHz to 1 MHz. The speed of light divided by the highest frequency, 30 MHz, results in the shortest wavelength the LCR meter and CNT yarn will experience, namely 10 meters—significantly larger than the entire circuit. We can safely assume constant current everywhere at any given instant and the current’s wave nature, such as impedance mismatch reflections, may be neglected. Figure 30 shows the attached factory made test fixture, which electrically connects the CNT yarn ends to the LCR meter. Also, resting on top the LCR test fixture, a low loss polyurethane scaffolding loops the CNT yarn from one test lead to the other.

![Image](image1.png)

Figure 30. The left two pictures show the factory made test fixture that housed and shielded the test leads from each other. The white polyurethane strip looped from one test lead to the other and supported the long pieces of CNT yarn we tested. On the right shows both LCR meters that allowed us to cover a range from 20 Hz to 30 MHz.

In order to get consistent results, where both LCR meters agreed over the overlap region, two techniques proved essential. First, we learned that we required a factory made test fixture, connected onto the LCR meter itself, to explore the frequency range under
consideration. At the beginning of the study, impedance measurements were executed simultaneously, and erroneously, with the resistance versus temperature measurements in the vacuum chamber--approximately two meters from the LCR meter. We connected the LCR meter to the displaced sample by special shielded coaxial cables and applied the necessary open/short corrections. With these measures, standard operations for other groups that use the system, the LCR meters yielded anomalous results—even for everyday circuit components such as a resistor. The CNT yarn, copper wire, and standard resistors, being maximum 5 cm long, exhibited significantly smaller inductance than the long wires used to measure it, which made it difficult to extract a physical reactance. Also, within the vacuum chamber, stray capacitances hindered accurate measurements. We made the decision to separate the impedance measurements from the vacuum chamber and measure the CNT yarn with the factory test fixture, on the LCR meter itself. The test fixture, connected to the LCR meter’s ground, shields the test leads from each other, other stray capacitances, and external electromagnetic radiation.

A load correction was learned to apply, in addition to the usual open and short corrections before measurement. An open measurement measures the impedance versus frequency when we remove the device under test (DUT). Even in this open configuration, a residual, albeit very resistive, connection between test leads exists, as well as setup capacitances and inductances, that the instrument must account for. In addition, the short correction, a conductive metal shorts the test leads and impedance measured again. Initially, we only used these open and short corrections and both LCR meters disagreed over the overlap region. In order to ensure the LCR meters agreed, we realized we required a load correction. With the load correction, we measured a device with known
impedance, in this case a precision resistor. We minimized the resistor’s inductive loop by pushing the resistor as close as possible to the test leads and minimized the resistor’s reactive contribution. With this minimization, we could safely assume the precision resistor only contributed the resistive part we know. We entered the impedance of the load, short, and open corrections, as well as DUT measured impedance, into equation 8 below to calculate a corrected DUT impedance [31].

\[
Z_{\text{DUT (Corrected)}} = \frac{(Z_{\text{Short}} - Z_{\text{DUT (Measured)}})(Z_{\text{Load (Measured)}} - Z_{\text{Open}})}{(Z_{\text{DUT (Measured)}} - Z_{\text{Open}})(Z_{\text{Short}} - (Z_{\text{Load (Measured)}}))} Z_{\text{Load (Actual)}}
\]  

(Eq 8)

For a given frequency, \( Z \) is the complex impedance for the specified aspect of the measurement. After these corrections were applied, the LCR meters agreed nicely over the overlap region.

We prepared several different lengths of all three CNT yarn types in order to uncover trends that scale with length. First, we silver painted cleaned copper leads to the CNT yarn ends and allowed them to dry overnight. Before measurement, we adjusted the radius of the polyurethane scaffolding to accommodate the CNT yarn length without significant slack or deformation of the loop shape. The scaffolding was necessary to keep a consistent loop where the we could calculated the expected loop inductance and reactance. Left to itself, CNT yarn tended to bunch up and twist. For the impedance measurements, the CNT yarn was unaltered and exposed to ambient room conditions, such as oxygen and water vapor.
2.2.3 Results and Discussion

First, we measured a nickel chrome wire, 30 cm long/.3 mm diameter, to establish an impedance baseline of an everyday, solid wire. We selected nickel chrome specifically because of its high resistivity, unlike copper wire, and more similar to the CNT yarn under test. The nickel chrome, however, measured around four Ohms while the CNT yarns typically hovered around hundreds of Ohms. Figure 31 below shows the real and imaginary parts of the nickel chrome wire impedance.

![Graph showing resistance vs. frequency for nickel chrome wire](image)

Figure 31. For the nickel chrome wire, the resistance is nearly frequency independent up to one MHz, where skin effect begins to set in.
Figure 32. For the nickel chrome wire, the measured reactance closely follows the modeled reactance.

The resistance appears constant until one MHz where the resistance starts to climb rapidly. At 20 MHz, the resistance increased by 5%. This rise resembles the skin effect, where higher frequency pushes current to the surface of conductor. Due to the resistive nature of the nickel chrome wire, the skin depth does not approach the diameter of the wire until 1 GHz and equations for AC resistance may not be applied to see if it fits the data above.

The nickel chrome wire reactance follows the behavior of an inductor, where reactance increases linearly with frequency. The black lines represent the calculated reactance of a loop of wire (top black line) and a straight wire with comparable dimensions to the nickel chrome wire. At these frequencies considered, the differences between both models are minor. The data follows these models nicely and, perhaps,
begins to diverge at the higher frequencies due to high frequency current moving to the surface and lowering the wire’s actual inductance.

\[ Im[Z_{loop}] = i \omega L_{loop} = i \omega (\frac{8 \pi r}{a} - 2) \]  
\[ \text{(Eq 9)} \]

\[ Im[Z_{wire}] = i \omega L_{wire} = i \omega \left( \frac{u_0 \pi l}{4a^2} - \frac{3}{4} \right) \]  
\[ \text{(Eq 10)} \]

Where \( Z \) is impedance, \( L \) low frequency inductance, \( \omega \) angular frequency, \( r \) loop radius, \( a \) wire diameter, \( l \) wire length, and \( u_0 \) magnetic constant. Overall, with the constant resistance and linear reactance, the nickel chrome wire follows a lumped circuit model of a series resistor inductor.

Next, we measured several different lengths of floating catalyst CNT yarn. Figure 33 shows the real and imaginary parts of the measured impedance below.

Figure 33. For all the various lengths of floating catalyst CNT yarn considered, the resistance remains constant with frequency. Beyond 10 MHz, there appears to be the start of a resistance drop, but the effect is within error bars. We will explore beyond this frequency range with more advanced measurement techniques.
Figure 34. The measured reactance also follows the expected reactance from an everyday wire of comparable dimensions. The black line depicts the expected reactance of the longest piece considered.

For all lengths considered, the resistance remained constant with frequency from 20 Hz to 30 MHz. The resistance seemingly begins to slope downward around 20 MHz, but this dip falls well within the error bars. Further investigation below will explore this potential trend. At first glance, the fact that resistance remained constant all the way to 30 MHz seems interesting. Due to the skin effect, the resistance should climb with frequency as we witnessed with the nickel chrome wire. At worse case, the CNT yarn behaves like a material without any AC mitigating effects. For the floating catalyst yarn, with approximate diameter 50 µm and resistivity .001 Ω cm, the skin depth does not approach the diameter until 1 GHz. Considering we are nearly two orders of magnitude less in frequency, we should not be surprised the resistance remained constant.

The reactance of the various lengths of floating catalyst yarn resembles the behavior of the nickel chrome wire. As the plot illustrates, the longer the piece measured,
the greater the inductance and steeper the reactance curve. For the longest piece measured, we calculated its expected inductance and reactance as shown with the black solid line. As shown, the expected reactance follows the measured reactance closely. Overall, like the nickel chrome wire, the floating catalyst CNT yarn follows a series resistor inductor model—at least for the frequency range considered.

Next we measured the forest grown CNT yarn. Figure 35 below shows the real and imaginary parts of the measured impedance below.

![Graph showing measured impedance](image)

Figure 35. The resistance of the forest grown CNT yarn is also frequency independent, with a similar appearance of a drop after ten MHz.
Figure 36. For the forest grown CNT yarn, the measured reactance is about five times greater than the expected reactance.

The resistance behavior resembles the floating catalyst CNT yarn—frequency independent with a slight dip well within the error bars. Investigation explained later will explore this dip region. The reactance, however, deviated strongly from the expected reactance as shown below.

The reactance scales linearly with frequency, and along with the constant resistance, the lumped circuit that best fits this data is the series resistor inductor. The only difference, however, is a reactance scaling factor five times greater than expected—implying an inductance five times greater than expected. We calculated the expected inductance for a loop as well as a straight wire, in both the DC and high frequency limits. The changes in inductance with these different models, however, only differed by a few percent and does not account for the fivefold increase.

There are two possible explanations for this inductance increase. One, there could be a lot of left over catalyst increasing the overall permeability of the material. The
producers, however, claim that the contamination is less than three percent by weight. Considering that floating catalyst CNT yarn is known to have a significant amount of leftover catalyst and the inductance effect is not present in this CNT yarn, higher permeability due to magnetic materials is not a likely scenario. Two, the forest growth CNT yarn is highly twisted with fifteen turns per millimeter. Possibly, the azimuthal component of the twisted yarn is producing a higher magnetic field than normal. Further testing and modeling may confirm this hypothesis.

Finally, we measured the impedance of the super acid solution spun CNT fiber. The resistance of this CNT fiber also remained constant up to our limit of 30 Mhz. Unlike the other bulk CNT yarns above, it lacks the mysterious resistance dip at the end. The measured reactance, as shown below, however, is off by a factor of 2 to 2.5—just like the forest grown CNT yarn.

For the floating catalyst and forest grown CNT yarn, apparently, the resistance begins to drop off after 20 MHz. The change in overall resistance typically amounted to a few percent and remained well within error bars. Potentially, however, this could signal the start of a trend. What was required was a network analyzer to measure the impedance beyond 30 MHz.

The frequency range and beyond was studied where the slight minimum in resistance occurred. Rather than using an LCR meter, that measures the ratio between voltage and current for a particular frequency, a network analyzer was used that operates on a completely different principle. With the network analyzer, a pulse, containing a continuum of frequencies, travels through the DUT and the network analyzer measures
the magnitude of reflected and transmitted frequencies. From these reflected and transmitted components we may determine impedances beyond the frequency ranges of other measurement devices.

As with the LCR meter, we still performed the open, short, and load corrections on the network analyzer. Due to the particular setup of this network analyzer, as shown in Figure 37 below, the test leads of the CNT yarn were placed really close together—significantly opening up the possibility of setup capacitive coupling that could give a false positive. In the LCR meter, we averted this problem by electromagnetically shielding the test leads from each other. With this setup, an instrument ground was not available so this shielding was not an option. Also shown in Figure 37 below, black plastic caps maintained the consistency of the CNT yarn loop.

![Graph](image-url)

Figure 37. For the super acid solution spun CNT fiber, the resistance is frequency independent up to 30 MHz.
Figure 38. The measured and expected reactance disagrees by a factor of two.

Figure 39. The left picture demonstrates how the network analyzer measures the CNT yarn. As shown on the right, we performed the short correction where we measure the impedance of a copper strip shorting out the test leads.
Figure 40. For the floating catalyst CNT yarn, the network analyzer shows us the resistance does not drop at the range the LCR meter suggested. The drop near 100 MHz seems to stem from the circuit setup rather than the material property itself.

Figure 41. As measured by the network analyzer, the reactance of the floating catalyst CNT yarn—still scaling linearly with frequency.

Figure 42 below shows the resistance and reactance as a function of frequency up to 100 MHz. With the exception of some kind of resonance near 80 MHz, the resistance
up to then remains constant with frequency and the reactance increases linearly—suggesting the standard series resistor inductor model. Thus, the small dip from the LCR meter is not the start of a trend, but measurement error for the floating catalyst CNT yarn. The resonance at 80 MHz does not seem to be a material property in that the same resonance occurred when we put an equivalent resistor in its place.

Figure 42 below shows the resistance and reactance of the forest grown CNT yarn. At the region where the dip occurred with the LCR meter, the resistance remains constant with the network analyzer. Thus, it seems like for the forest grown CNT yarn, the LCR meter resistance dip was instrument error too. The reactance, however, dives to the negative side and, again near 80 MHz, the resistance starts to plummet. This behavior is indicative of a dominant capacitive effect. When placing an equivalent resistor however, we observe the same behavior. Although far from conclusive, these high frequency effects seem similar for both the CNT yarn material and the resistors—which points to instrument setup and not actual material properties that lead to resistance drops.

Figure 42. As measured by the network analyzer, resistance as a function of frequency for the forest grown CNT yarn—similar to the results above.
Figure 43. The negative reactance is indicative of a capacitive effect. Most likely, this capacitance is from the setup of the circuit and test leads.

All three forms of CNT yarn behave like a resistive wire with a constant resistance, at least up to 30 MHz. Interestingly, forest grown CNT yarn has an unusually high reactance that points to an unusually high inductance. Most likely this inductance comes from the twist in the CNT yarn itself. For physical reasons, however, a resistance drop should occur at some point. After all, others have found resistance drops with other bulk CNT materials in the GHz range.
3.1 Summary

In summary, the resistance versus temperature and resistance versus frequency of three types of bulk CNT materials were tested. With the resistance versus temperature fitting, we learned that floating catalyst CNT yarn behaved like crystalline graphite with a temperature minimum. We also learned that a vast majority of this resistance comes from the junctions between CNTs, rather than the CNTs themselves. For the forest growth CNT yarn and super acid solution spun CNT fiber, we learned it behaved like amorphous carbon with a resistance that decreases monotonically with temperature. With all these materials, we saw the drastic change in resistance during the first temperature sweep in vacuum, indicating the significant effect of oxygen doping when exposed to ambient conditions.

We explored the impedance of all three materials and saw, at least at the frequency ranges considered, the bulk CNT materials behaved like everyday wires that can be modeled with a series resistor and inductor circuit. The forest grown CNT yarn, in particular however, possessed an unusually high inductance. Possibly, this high inductance is due to magnetic material content, but more likely results in the significant twist in the CNT yarn.
3.2 Future Work

Measuring resistance versus temperature is a good way to characterize a bulk CNT material. In general, as the overall properties improve and the material becomes more metallic, 1) a resistance minima develops and 2) the minima shifts left to colder temperatures. It would be very interesting exposing these materials to post processes, such as high temperature annealing and temperature doping, and seeing if these trends would develop. As indicated in Figure 15, the conductivity of bulk CNT materials has a long way to go before it reaches the best of carbon fiber, let alone conductive metals such as copper.

Literature reports that at the GHz range the resistance should drop significantly. It would be interesting exploring this regime with the bulk CNT materials. At this point, however, the wavelength of radiation begins to reach the length of the circuit and more sophisticated means must be used to measure impedance of the device under test. In addition, the bulk CNT materials should also perform better than regular metals under changing magnetic field. This application would be particularly useful for Nuclear Magnetic Resonance where induction coils deal with rapidly changing current.
REFERENCES


32 Kozlowski, G., private communication.