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Jack Alvarenga

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Carbon Nanotube Materials for Aerospace Wiring

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August 24, 2010
Submitted in partial fulfillment of the requirements for the degree Master of Science

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Carbon Nanotube Materials for Aerospace Wiring

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We, the undersigned members of the Faculty of the Rochester Institute of Technology, certify that we have advised and/or supervised the candidate on the work described in this thesis. We further certify that we have reviewed the thesis manuscript and approve it in partial fulfillment of the requirements of the degree of Masters of Science in Materials Science & Engineering.

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ABSTRACT

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Title: Carbon Nanotube Materials for Aerospace Wiring

With large amounts of time and money invested in the advancement of aerospace structures, the performance and reliability are crucial factors in the development of new components to extend the lifetime of these spacecrafts. Wires composed of long, highly aligned, and defect-free carbon nanotubes (CNTs) could have a great impact on aerospace, military, and industrial applications which require lightweight and durable electrically conductive materials. Carbon nanotubes represent an ideal material which is not only electrically conductive, but also exhibits resistance to oxidation, radiation tolerance, and mechanical robustness. Highly conductive bulk carbon nanotube wires were drawn to meter lengths using a drawing die process. A series of solvents were investigated as potential lubricants to improve the process as well as the electrical and mechanical properties of the resulting wires. Inorganic and organic chemical doping was used in conjunction with densification to increase the electrical conductivity of the wires, achieving a maximum conductivity of $1.3 \times 10^6$ S/m. Temperature dependent electrical conductivity measurements were recorded to evaluate the fundamental electrical conduction mechanism in CNT wires resulting from the doping and densification processes. These measurements indicated that the electron tunneling barrier between adjacent CNTs can be drastically reduced by ionic doping and densification. Furthermore, a novel technique of contacting CNT wires to metals via ultrasonic welding was reported with mechanical and electrical characterization of the welds achieved. Lastly, real world demonstrations of the power and data transmission capabilities of these CNT wires were constructed and tested, specifically a USB cable and coaxial wires.
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Introduction

As space exploration and reconnaissance continues to grow, advanced lightweight and reliable alternatives to conventional aerospace materials are being researched and implemented. With costs of launching a heavy lift system in low Earth orbit ranging between $6000 and $20000 per kilogram\(^1\), and approximately $36000/kg for geosynchronous orbit\(^2\), revision of any component in the structure presents an opportunity for mass savings. As with most other industries these days, the aerospace industry is turning towards nanotechnology to produce not only lighter, but better performing components.

In 2005, emerging nanotechnology was incorporated into more than $30 billion in manufactured goods (more than double the previous year). By 2014, it has been projected that $2.6 trillion in global manufactured goods (approximately 15% of the total market) will incorporate nanotechnology.\(^3\) Polymer matrix composites with embedded nanoparticles are an ideal example of the realization of nanotechnology in the aerospace industry. These nanocomposites have been applied at numerous locations within the hierarchical composites to improve specific thermal, mechanical and electrical properties.

The extraordinary properties of carbon nanotubes have already attracted the aerospace industry, resulting in a plethora of possible applications.\(^4\) Electrostatic charge-dissipating adhesives and coatings could be improved by the incorporation of CNTs as percolation networks in resin between conductive fibers. Electromagnetic interference (EMI) shielding enclosures could be comprised of CNT films that can effectively absorb broadband frequencies instead of aluminum. Mechanically, robust structures can be reinforced with high elastic modulus CNT yarns/sheets.
Alternatively, the need for advanced wiring concepts that can minimize ohmic losses while increasing mechanical stability in space systems is paramount. The aerospace industry is continually interested in reducing inactive spacecraft mass as a way to reduce payload costs and boost hardware efficiency. In general, the wire harness components are approximately 10% of the total spacecraft mass. Historically, this has been limited to the selection of a few common materials (e.g. copper, silver, and aluminum) providing sufficient, but not completely ideal, properties. Recently, the discovery of carbon nanotubes, and subsequent commercial-scale production, opens up the possibility to push the frontier of materials development such that advanced wiring concepts can begin addressing many of these present-day challenges.

As a short-term goal, it is imperative that new materials electrically outperform conventional metals on a per density basis. The metric of specific conductivity (the electrical conductivity divided by the bulk density) is often used for the comparison of dissimilar materials. To assist in determining the electrical conductivity values required for bulk CNTs to surpass the performance of several metals, Figure 1 illustrates the specific conductivities of CNT materials of varying densities; several metals are marked as horizontal lines for comparison. When taking into account the density of the wiring materials in question, copper with a density of 8.92 g/cm³ yields a specific electrical conductivity of 6.6 x 10⁴ (S·cm²/g). Assuming a density of 0.8 g/cm³ for pure and aligned SWCNTs, based on the literature,⁵ yields a specific conductivity for the SWCNTs of 9.6 x 10⁵ (S·cm²/g) (Figure 1). Thus, there exists a nearly 15X improvement of the specific conductivity when comparing pure SWCNT wires to copper.
Figure 1: Plot depicting electrical conductivities required from SWCNT samples at varying densities in order to exceed the performance of conventional wiring metals (values derived from CRC Handbook of Chemistry and Physics).

Furthermore, there are terrestrial applications which can benefit from the potential of carbon nanotube wires. Several years ago, Nobel Laureate Richard Smalley proposed the “Terawatt Challenge”, a prioritized list of problems facing the world today. He argued that energy was the key issue at hand. Cheap, and preferably renewable, energy would be crucial to solving the rest of the world’s problems, from water pollution to over-population. Energy assumes the dominant role in establishing the quality and preservation of our environment, the prevention of disease, and so on, down the list of global concerns. Aside from finding new, reliable sources of energy, Smalley also highlighted the need for innovation in transmitting large amounts of electrical power (~100s of gigawatts) across the grid. Existing high-voltage power
lines can carry electricity for 1500 miles with fairly low losses, but they only carry about 1 gigawatt of power. To maximize our benefits from alternative sources of energy, alternative wiring materials options, such as carbon nanotubes, to improve power transmission warrant further investigation.

**Carbon Nanotube Properties**

Carbon is a truly diverse element. With its ability to form single, double, and triple bonds, it is widely used in the synthesis of complex organic molecules. For many decades, only two basic crystallographic forms were recognized for carbon: diamond (which is a large band gap insulator) and graphite (which is a semimetal – electrically conductive along its plane due to electron delocalization). With the discovery of the C_{60} buckyball, it became evident that other forms of carbon exist at the nanoscale. In 1991, tubular carbon nanostructures were observed in the soot from an arc discharge experiment. This discovery of carbon nanotubes has been received with growing interest and has sparked global research, including this work, on these novel materials.

The synthesis of CNTs can be accomplished by several methods, each offering different distributions of purity, diameter, and chirality types. The original discovery of CNTs was with carbon soot generated by the arc-discharge method. This method applies high voltages across two metal-doped graphitic rods in the presence of an inert atmosphere to develop a vaporized carbon plume. CNTs have also been synthesized using a laser vaporization procedure, where a source laser (such as Nd:YAG, Alexandrite, etc.) is applied to a metal-doped graphite target under inert atmosphere and elevated temperatures. The resultant metal-carbon vapor generates a plume which, under flowing Ar(g), condenses outside of the furnace into a mixture of CNTs and
synthetic impurities. However, drawbacks exist for both the arc-discharge and laser vaporization methods, namely the extremely elevated temperatures for synthesis and the high entanglement of CNTs. In an attempt to develop a synthetic procedure that could enable mass production (kg – ton) of CNTs, Smalley et al., pioneered the HiPco process. This method employs passing CO$_{(g)}$ along with catalytic amounts of Fe(CO)$_5$ through a reactor chamber at high temperatures and pressures. One significant advantage of this process is the continuous flow that allows for proposed reproducibility and scale-up potential. Several of the aforementioned limitations have been addressed via an alternative method, namely chemical vapor deposition (CVD) synthesis. Generally, chemical vapor deposition introduces a carbon feedstock gas over a catalyst-supported substrate at moderate temperatures. This method has established a certain degree of control over helicity, diameter, and growth orientation. Also, the ease of large scale CVD synthesis allows vast quantities of CNTs to be synthesized in a more cost-effective manner and has resulted in recent commercialization by Nanocomp Technologies, Inc. Yet, current CVD techniques still face limitations on the purity and defects associated with synthesis.

Each type of carbon nanotube, single wall or multi-wall, exhibits unique and useful properties for both basic science and applied technology. The commercial CNT material, which is the focus of this thesis project, is comprised of both single wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). Although these different types were inseparable and not studied independently in this work, a brief overview of the individual properties of SWCNTs and MWCNTs will be described to highlight their advantages and the differences between the two types.

The structure of a SWCNT is best envisioned by taking a single sheet of graphite (graphene) and rolling the sheet such that it forms a crystalline, seamless cylinder. Each
generated tube incorporates hexagonal benzene rings along the cylindrical shaft, carbon atoms being sp$^2$ hybridized. The manner in which the benzene rings orient along the nanotube structure determines the unique chirality-types associated with SWCNTs, upon which their electrical and optical properties will vary based on helicity. The sp$^2$ hybridization of carbon atoms in a graphene sheet displays interesting conducting properties based on the electronic band structures. The electronic state at the Fermi level is unique for graphene because the structure displays a semimetal behavior. Semimetal band structure can been understood as a crystal lattice where electrons can backscatter in the lattice like typical semiconductors, or propagate through the lattice similar to metals. Graphene exhibits both properties, dependent on the angle where electrons scatter in the lattice. Consequently, SWCNTs will show similar electronic properties based on the chirality, or angle of formation from the rolled up graphene sheet. Derived from their symmetry, SWCNTs exhibit various diameters ranging from 0.4 - 1.4 nm. Similarly, MWCNTs are composed of concentric layers of graphene sheets stabilized by Van der Waal’s interactions, with spacing between coaxial layers equal to 0.34 nm. Current-induced breakdown has been used to selectively remove outer layers in a MWCNT, allowing successive shells to be characterized, indicating both conducting and semiconducting nanotubes. MWCNTs have been observed with diameters ranging from 2 - 100 nm and lengths from 1-1000 microns.

In metallic CNTs, electrical current is carried along the surface, in the same manner that current flows over metallic wires. The majority of the current flows along the outermost nanotube layer for MWCNTs. Theoretical calculations have predicted that ballistic conductance would occur along a defect-free metallic CNT; meaning that in the absence of any electron scattering, the resistance would not vary along the length of the CNT. The ballistic resistance in metallic SWCNTs has been estimated to be 6.45 k$\Omega$, while the resistance of MWCNTs is...
slightly higher at 12.9 kΩ. The strong covalent carbon-carbon bonding in CNTs also provides them with high resistance to electromigration, a current-assisted diffusion process. For very small diameter metal wires, this effect can cause failure at relatively low currents, resulting in a current-carrying capacity of $\sim 10 \text{ nA/nm}^2$. In defect-free carbon nanotubes, the current-carrying capacity can exceed 10 $\mu\text{A/nm}^2$, also due in part to the absence of electron scattering and resistive heating.

Single wall carbon nanotubes not displaying metallic symmetry offer a different set of properties, closely resembling silicon in standard p-type metal-oxide-silicon field-effect transistor (MOSFET) applications. These semiconducting SWCNTs can be used as transistors, where application of a negative bias causes conduction via hole carriers. Researchers have indicated that adsorbed species on the SWCNT surfaces are responsible for p-type doping, while in certain instances, atoms like potassium can orient to donate electrons to the SWCNT, resulting in n-type behavior. Overall, CNTs offer tremendous potential for electronic applications, each directly related to the unique properties exhibited by both metallic and semiconducting CNTs during synthesis.

In addition to electronic properties, CNT structure and sample morphologies are also being widely investigated for their physical characteristics, in particular the potential for composite applications. The high aspect ratios for the CNTs suggest utility as reinforcements in polymer and ceramic composites. In addition, the Young’s modulus has theoretically been predicted and experimentally verified to equal $\sim 1 \text{ TPa}$. Tensile strength for individual SWCNTs has been estimated to equal 22 GPa. These reports correlate to strengths 10-100 times that of steel, providing additional evidence for novel SWCNT materials. Structural properties of MWCNTs include the ability to be twisted and “kinked,” before elastically...
returning to original shape. Research indicates that these kinks may potentially lead to functionalization of the carbon nanotube sidewalls, increasing chemical reactivity.\textsuperscript{27}

Although outside the scope of this work, carbon nanotubes also have thermal properties that make them desirable for many applications. Several simulations have suggested that the thermal conductance of CNTs is in the range of 1000 – 6600 W/m-K, comparable to the thermal conductivity of diamond.\textsuperscript{28} The exceptional predicted thermal conductivity of CNTs makes them appealing for applications where heat needs to be dissipated quickly, such as in cooling integrated circuits.

While these materials possess properties that would be desirable in a plethora of applications, several challenges will need to be addressed prior to their implementation. One of the main obstacles with these novel materials is organizing individual CNTs into a form factor which allows the exploitation of these preferred properties. Another concern is the discrepancies in experimental conductivity values reported in literature (Figure 2). Ultimately, the future of CNTs beyond the realm of nanotechnology will be determined in part by the successes of emerging technologies making use of bulk CNTs.
Figure 2: Brief summary of reported electrical conductivities for bulk CNT materials (including results of doping studies and NPRL typical values).

**Carbon Nanotube Fibers**

Due to the remarkable mechanical and electrical performance observed in individual carbon nanotubes, much interest has been generated in transferring these properties to macroscopic structures. Due to the anisotropic natures of CNTs, wires or fibers are a logical evolution for these materials.
For use in high strength applications, CNTs have been incorporated into composite materials as fiber reinforcements, which strengthen the material by carrying loads transferred to the fibers by shear stresses at the matrix interface. Nanotube-based composites have been reported that are stiffer, stronger, harder, tougher, and more wear resistant than the parent matrix material.\textsuperscript{22}

In a more recent approach, carbon nanotube-polymer composite fibers can be produced via a wet-spinning coagulation process.\textsuperscript{29} Coagulation spinning is widely used for making Kevlar, acrylic, and poly(acrylonitrile) fibers. In this adapted method, a kinetically stable CNT dispersion is created with the aid of a surfactant (sodium dodecyl sulfate, SDS, in this particular case). The surfactant is able to form a micelle structure around individual CNTs, thus preventing re-bundling. This dispersion is then injected, via a syringe pump, into a co-flowing stream of 5% polyvinyl alcohol (PVA) in water. Under these conditions, flow-induced alignment of the CNTs is expected in the direction of the fluid velocity. Coagulation of the dispersion occurs as the PVA, which does not provide an efficient stabilization against van der Waals attractions, displaces the SDS. Simultaneously, the extruded material undergoes solvent loss, solidification, stretching and nanotube alignment to form a final solid fiber with high CNT content (>60%). The load transfer between CNTs and PVA chains in these fibers is extremely effective (tensile strengths up to 3.2 GPa\textsuperscript{30}) when compared to CNT fibers coagulated without PVA. Unfortunately, these composite fibers do not provide a substantially improved modulus or tensile strength compared to pure PVA fibers. In addition, the presence of the polymer between the CNTs compromises the electrical properties of the fiber. Sacrificing some of the mechanical performance of the fibers, the electrical properties can be improved by stretching the as-spun fiber (5 x 10\textsuperscript{-1} S/m) or more drastically by completely removing the polymer binder through an
annealing treatment in hydrogen at 1000°C (2 x 10^4 S/m).\textsuperscript{31} Coagulants other than PVA have been investigated with this method to produce polymer-free, electrically conductive fibers, but the extremely weak mechanical properties of these fibers limit their applicability.\textsuperscript{32}

Despite the tremendous advancements in the mechanical strength of these CNT composite fibers, the widespread use of binding polymers negates the high electrical conductivity of the CNTs. For electronic applications, it appears as though producing macroscopic materials comprised solely of CNTs is the most viable route to take advantage of their unique properties, such as ballistic electron conduction. To date, several research groups have modified processing techniques inspired by other industries to create pure CNT fibers.

Similar to the previously detailed surfactant-based wet-spinning technique, CNT fibers have been extruded from high concentration dispersions of CNTs in superacids (e.g. polyphosphoric acid, 102% sulfuric acid). These strong acids are inexpensive solvents that are already commonly handled in industry, having been used in the commercial production of high performance synthetic fibers composed of rod-like polymers.\textsuperscript{33} Currently, superacids are presented as the only natural solvent for CNTs, in that they do not require sonication. SWCNTs dissolved spontaneously because they become protonated by the superacid; the ensuing electrostatic repulsion counteracts the attractive van der Waals forces.\textsuperscript{34} At high enough concentrations of CNTs, a fully liquid-crystalline solution is formed from which a highly aligned fiber can be spun. Liquid crystals are systems that possess a degree of long-range molecular orientation, but lack the complete three-dimensional crystallinity of a solid. Replicating conventional rigid rod polymer wet-spinning techniques, the CNT dispersion coagulates in a precipitation bath (e.g., water, dilute sulfuric acid, ether). At this point, the solvent diffuses out of the fiber into the bath, thus solidifying the extruded fiber. These as-spun fibers possess a high
electrical conductivity ($8 \times 10^5$ S/m) due to the strong redox doping effect of bisulfate from the acid suspension, but a very low tensile strength of 0.116 GPa.$^{35}$

Carbon nanotube yarns, 10-20 cm in length and 5-20 µm in diameter, were first observed as a byproduct of the pyrolysis of hexane (carbon source), ferrocene (iron catalyst source), and thiophene (sulfur compound known to promote carbon-hydrocarbon reactions, especially in the presence of iron).$^{36}$ Without the influence of a substrate, CNTs growing from these floating catalyst particles form long strands, formed and held together by van der Waals forces. These ropes had promising electrical conductivity ($1.4 \times 10^5$ S/m) and tensile strength (0.8 GPa), motivating further efforts into spinning the CNTs into continuous, uniform fibers as opposed to isolated strands. Building upon the solid-state spinning techniques used to assemble natural fibers, such as cotton and wool, into a continuous yarn, scientists have successfully fabricated CNT yarns in a similar manner.

After witnessing that fiber formation can occur directly in the reaction furnace instead of other post-processing techniques, the “Cambridge Method” (as it is commonly referred to) was developed. In this one-step process, the CNT aerogel formed in the CVD reaction zone is mechanically drawn into a continuous fiber with no apparent length limitation, as long as feedstock materials continue to flow into the system.$^{37}$ This synthesis set-up can also be used to produce CNT films depending on the wind-up geometry used to capture and wind up the aerogel onto the rotating collection spindle. The carbon source was critical in the ability to dry-spin CNTs; with carbon sources containing oxygen (i.e. ethanol, acetone) being successful, whereas aromatic hydrocarbons (i.e. benzene, hexane) were not. Replication of this method is not without its drawbacks, as the use of pure hydrogen as the carrier gas is a safety concern but also believed to be crucial to the process. Experimentally, a high hydrogen flow rate was found to suppress
amorphous carbon formation, whereas the removal of hydrogen (replaced with argon) led to the precipitation of particulate carbon rather than CNTs. For fibers created with this method, the highest electrical conductivity was measured to be $8.3 \times 10^5$ S/m (slightly higher than the typical value for carbon fibers). Mechanical strengths of the fibers were moderate, ranging from 0.10 to 1.0 GPa depending on synthesis conditions. By drawing the CNT aerogel at various winding rates, different levels of CNT orientation and fiber density were attained, thus resulting in a range of mechanical properties.\textsuperscript{38}

A similar technique involves fiber spinning from a vertically-grown, super-aligned CNT array.\textsuperscript{39} Serendipitously, while attempting to pull out a bundle of CNTs from an aligned array (several hundred micrometers in height) a continuous yarn of pure CNTs was obtained instead. Once again, due to the van der Waals interactions between CNTs, as carbon nanotubes are being pulled away manually, they tend to carry adjacent CNTs with them and so on. The drawing process instills a high degree of alignment along the pull direction, which becomes the fiber axis. Similar to the Cambridge Method, once the process has been initiated by contacting a sharp, roughened probe to the side of the array, a spindle can be used to twist the CNT yarn. Yarns produced in this manner can have several benefits. Perhaps most significantly, the separation of CNT synthesis and processing grants the user greater control over the CNT length (with longer tubes producing stronger fibers).\textsuperscript{22} In addition, the fiber parameters can be controlled during the spinning process. Carbon nanotube yarns spun from this process have been found to have toughness nearly 100 times higher than that of carbon fibers and roughly 30 times higher than Kevlar.\textsuperscript{40} Although this process offers intriguing results and seems rather straightforward to replicate, the conditions for synthesis of “spinnable” CNT arrays are rather precise. Researchers have emphasized bundling within vertically grown CNTs and the disordered regions on the top
and bottom of the array, claiming that they aid the interlocking of CNTs.\textsuperscript{41} Conversely, other studies have found that the absence of amorphous carbon can still yield spinnable aligned CNTs.\textsuperscript{42} In addition, recent studies into the roles of catalyst, substrate, temperature, gas flow rates and reaction time experimentally derived optimum conditions, but they concluded that there is no one key factor for CNT spinnability and no other identifiable characteristic that can help distinguish between a spinnable and a non-spinnable array.\textsuperscript{43} Arrays ranging in height from 80 to 900 µm, CNTs from 10 to 7 nm in diameter, and areal densities ranging across an order of magnitude can be spinnable or not.

Considering that carbon nanotubes often draw comparisons to extremely strong and stiff polymer molecules, it should be no surprise that the first processing routes developed for CNTs heavily borrowed concepts from polymer fiber-processing techniques. Likewise, the electrical similarities between CNTs and metals have recently resulted in the translation of processing methods. A low-cost drawing die method has been reported to densify and align as-produced disordered CNT films into macroscopic wires.\textsuperscript{44} The drawing was carried out through diamond drawing dies with decreasing pore diameters in sequence (18 dies in total ranging from 1.2 to 0.2 mm) using deionized water as the drawing lubricant. Whereas the aforementioned techniques triumphed in making thin fibers (10-100 µm), this method offers an effective means of precision controlled diameter wires with a wide range of achievable dimensions. Bearing in mind that the primary focus of the publication was to argue CNT alignment through die drawing with x-ray diffraction patterns, until now, various characterization and optimization opportunities have gone unanswered. With an estimated room temperature conductivity of $5 \times 10^4$ S/m and no mechanical properties reported, the prospect of CNT wire drawing using a series of dies will benefit from additional measurements and further investigations.
The present work builds upon this potentially revolutionary CNT wire drawing method by providing the first mechanical strength measurements for CNT wires created by this method, addressing the opportunity to apply various lubricants and chemical dopants during the drawing process for enhanced electrical performance, evaluating the stability of CNT wires in harsh environments, and demonstrating additional technology applications for these wires.

**Experimental**

As mentioned previously, interests in macroscopic assemblies of CNTs have led to the development of multiple techniques to produce thin CNT fibers (10-100μm). Both liquid and solid-state spinning techniques offer compelling results, but perhaps the most simplistic and controllable method for fabrication of robust, conductive CNT wires was reported by Liu et al. In this process, shear and compressive forces are applied to the bulk CNT material, which permanently packs the starting material into a favorable wire form factor.

When studying bulk CNT materials, it is reasonable to consider them as heterogeneous systems with multiple components, often including metal catalysts and air pockets in varying ratios dispersed throughout the CNT medium. Electrical characterization of these systems can be complex when one takes into account conductive and insulating nature of the individual components, the volume fraction of the components, and the morphology of the medium. Comparatively, previous studies have shown that axial compression of various graphite or carbon black powders can create solids of increased conductivity by effectively decreasing the air to graphite volume fraction.

Molecular interactions ideally form organized CNTs with a two-dimensional hexagonal close-packed structure. Taking into account the dipole-dipole interactions that limit how close two molecules can approach each other, the theoretical density of aligned CNTs in a bundle has
been reported between 1100 – 1500 kg/m³, depending on the diameter.\textsuperscript{48} Unfortunately, multiple bundles compose bulk structures, and vast void spaces tend to exist between these CNT bundles. As a result, the volume conductivity of bulk CNT materials is difficult to accurately evaluate due to the obstacles presented by the commonly ignored geometric factor related to these empty mesopores. The drawing die method can succeed in providing a means of creating robust and dense CNT wires, while granting an unexplored avenue for modifying its properties through chemical additives. The method also serves as a simple technique for creating compact wires where the measured cross-sectional area is more accurate in terms of assessing the true amount of material used for electrical conduction or load bearing.

In an effort to improve on the drawing procedure, this work investigated the use of long, commercially-produced CNT sheets alongside different lubricants for drawing meter-long wires with excellent electrical conductivities. Bulk CNT sheets possessing nearly constant areal densities were acquired from Nanocomp Technologies, Inc. Homogeneous strips (~2 cm wide) were cut along the length of the as-received CNT sheet (~1 m long) and tapered at one end to facilitate initializing the drawing process. The subsequent strips were then soaked for a period of several minutes in solutions to act as a drawing lubricant and also a chemical dopant in specified cases. After removal from the soaking solution, the wet ribbons were laid flat on a clean glass surface and manually rolled up into a cylinder. The cylinders were then hand-drawn through tungsten carbide dies of descending size from 1.20 - 0.35 mm (Figure 3). Thinner gauge wires can also be achieved by using a thinner (width or thickness) CNT ribbon, serving as an alternative to reported CNT yarns. Samples for testing were removed from the end of the drawn wire at varying degrees of densification and then dried in an oven at 200°C to remove any residual moisture before having their masses measured with a microbalance. Wire diameters
were measured using a digital optical microscope. Four point probe resistance measurements were taken along different lengths of CNT wire, while sourcing up to 100 mA of current.

![CNT Ribbon](image)

**Figure 3:** Tungsten carbide drawing dies (top left), schematic of radial densification ensuing from the drawing process (bottom left), images depicting CNT materials at various stages of the drawing process (right).

**Wire Drawing Background**

In the drawing process, the cross-sectional area and/or the shape of a tube or wire is reduced by pulling through a series of cone-shaped dies. Wire drawing is commonly performed at room temperature using a number of passes or diameter reductions through consecutively positioned dies. Tensile and compressive stresses created by the pulling force at the die exit result in the plastic deformation of the metal into its desired form factor. On occasion, certain metals require a number of annealing treatments to counteract the effects of strain hardening and increase the ductility of the product.
The earliest written account of wiredrawing is that according to Theophilus in 1122 A.D., in which he briefly describes a draw plate\textsuperscript{49}, “Two iron [plates] three fingers wide, narrow at the top and bottom, thin throughout and pierced with three or four rows of holes [of diminishing size] through which wires may be drawn.” With such an extensive history of use, great optimization of the process has resulted in the widespread use of wires in a multitude of products ranging from jewelry to musical instruments to automobiles to suspension bridges.

What began as a hand-powered process, today’s industrial drawing processes have evolved to a point where a previously rolled or extruded metal product can be pulled through a die at exit speeds upwards of several thousand feet per minute.\textsuperscript{50} Consequently, dies are manufactured with diamond or cemented tungsten carbide inserts which can be subjected to the severe conditions encountered during cold drawing. Despite enhanced performance compared to tungsten carbide, the use of diamond dies was historically restricted to smaller diameters due to low availability and high costs associated with large diamonds. But in the latter half of the 20\textsuperscript{th} century, a variety of synthetic polycrystalline and single-crystalline diamond die stocks became available, thus extending the prominence of diamond die materials. On the other hand, cemented tungsten carbide represents an economical option for wire-drawing dies of all sizes.

Despite being one of the oldest metalworking procedures, drawing allows smooth surface finishes and finely-controlled dimensions to be obtained along the length of the entire wire. But to achieve these results, proper lubrication is critical in wire drawing. Friction is an unessential component of the wire drawing process. Commonly, with metals, the lubricant is chosen for its ability to provide the lowest friction and prevent tooling abrasion. For high-speed drawing applications, the lubricant must also be able to dissipate the heat generated by friction. The aqueous or oil-based lubricant can be applied to the die inlet and/or the wire. In some cases, the
entire drawing setup can be submerged in a bath. This “wet-drawing” practice is typical of all nonferrous metals and steel wires less than 0.5 to 1.0 mm in diameter.\textsuperscript{51}

As expected, the widespread use of any newly developed materials is more likely if they are compatible with traditional or current manufacturing and processing techniques. In this case of drawing CNT wires, industries can benefit from the absence of a financial burden associated with new equipment.

**CNT Wire Characterization**

**Electrical Characterization**

In principle, the measurement methods for a material’s electrical conductivity can be divided into two categories, direct current (DC) and alternating current (AC) measurement methods. The main focus of this work is to measure, understand, and improve the DC conductivity of CNT wires fabricated via the drawing die method, with some proof-of-concept AC conductivity measurements for additional proposed applications.

The DC conductivity is determined by measuring the resistance $R$ and the dimensions of the uniformly-shaped conductor (length $L$ and cross-sectional area $A$).\textsuperscript{52} From these measurements the conductivity $\sigma$ is calculated using Equation 1

$$\sigma = \frac{L}{R \cdot A}$$  \hspace{1cm} (1)

The resistance is measured by a four point voltage-current method. An electric current $I$ is swept through a preselected range of values and the drop in voltage $V$ is measured across the sample (Figure 4). The resistance is then calculated according to Ohm’s law

$$R = \frac{V}{I}$$  \hspace{1cm} (2)
Once again, this method is applicable to materials of particular, uniform shape like cylinders or rectangular bars.

Figure 4: Current-Voltage sweeps for a KAuBr$_4$-doped CNT wire (addressed in “Doping Effects” section) with two different probe separations (13.7 mm and 18.1 mm); four-point probe station used for electrical measurements featured in inset.

For more complex geometries, different methods have been developed. For flat samples of arbitrary shapes (i.e. discs), the van der Pauw method can be used to measure the conductivity of arbitrarily-shaped samples without knowing the current pattern if the contacts are at the perimeter of the sample, the contacts are sufficiently small, and the sample is of uniform thickness without any isolated holes on the surface.$^{53}$ The use of four terminals ensures that the measured voltage does not include the voltage drop due to the current contacts. The van der Pauw method consists of two separate measurements of resistance, $R_{AB}$ and $R_{AD}$ where $R_{AB} =$
With these values, the conductivity can be determined by measuring the sample thickness \( t \) and solving the following transcendental equation for \( \sigma \):

\[
e^{-\pi t \sigma R_{AB}} + e^{-\pi t \sigma R_{AD}} = 1
\]

(3)

Figure 5: Illustration depicting two possible configurations for use in the van der Pauw method of calculating resistivity.

The main challenge in direct current measurements is establishing good electrical contact between the test material and probes. In many cases, the surface of a metal is covered by a thin oxide layer which must be penetrated for accurate measurements. This problem is generally overcome by the AC measurement method. In this method, alternating electromagnetic fields are created to penetrate the test metallic material, thus inducing an eddy current in the material. This effect is used in a way that the test material acts as a nearly ideal inductor. Depending on the magnitude of the eddy current, the non-ideal inductor shows magnetic loss. This field loss can be measured as the resistive part of the inductor, which can be detected to extract its conductivity.

Whereas a direct current will flow uniformly throughout the cross-section of a homogeneous wire, an alternating current of any frequency will gravitate towards the surface of the wire due to the skin effect. In other words, the skin effect limits the penetration of the eddy
currents into the conducting surface. This penetration depth $\delta$, or “skin depth”, can be expressed as

$$\delta = \sqrt{\frac{2}{2\pi f \sigma \mu_R \mu_0}}$$  \hspace{1cm} (4)

where $f$ is the AC frequency, $\sigma$ is the electrical conductivity, $\mu_R$ is the relative permeability of the conducting medium, and $\mu_0$ is the permeability of vacuum. This shows that the depth to which electromagnetic radiation can travel into a material decreases as the conductivity and the oscillation frequency increase. For pure copper, the skin depth is roughly 8.4 $\mu$m at the common power transmission frequency of 60 Hz.

For this work, four point DC resistance measurements were taken with a National Instruments Source-Measure Unit 4130 with customized LabView software. AC measurements performed with an Agilent Technologies E5071C ENA Series Vector Network Analyzer in the frequency range of 9 kHz – 4.5 GHz.

**Mechanical Characterization**

Conventional wiring materials are not commonly subjected to mechanical loads, but in aerospace applications the prospect of a multifunctional electrical and structural wire is appealing. The mechanical loading on materials in engineering applications can occur in a variety of situations. The loading may be static or dynamic, and then further categorized as tension, compression, shear, torsion, or bending. For brevity, only the dynamic tension performance of CNT materials was addressed in this work.

The mechanical loading action and the corresponding response of test materials can be analyzed by a stress-strain curve (Figure 6). This type of curve is obtained when a specimen is
loaded uniaxially and strain is obtained as a function of the load applied. Stress, a measure of the mechanical forces that are absorbed by of the material, is calculated by the mechanical load divided by the cross-sectional area of the sample. The strain represents the relative displacement of points within the material due to external forces and is simply calculated as the length displacement divided by the original test length. The slope of the linear portion at the beginning of a stress-strain curve is used to calculate the Young’s modulus of the material, a commonly reported metric in materials engineering.

![Diagram of stress-strain curve](image)

**Figure 6:** Illustration of a characteristic stress-strain curve outlining the significant areas for this work.

For this work, mechanical testing was performed on a TA Instruments Dynamic Mechanical Analyzer Model Q800 with an 18 Newton load cell for weaker CNT samples and an Instron Universal Testing Instrument Model 1125 with a 500 Newton load cell for stronger
samples. Fixed clamps tightened manually with a torque wrench were used to mount samples in the Q800, whereas pneumatic grips were implemented with the Instron testing. Wire diameters were measured with a digital optical microscope.

Mechanical testing of the received materials was conducted in the form of a 0.2 N/min force ramp until failure of CNT sheet strips measuring on average 9 mm in width and 60 µm in thickness. Experiments revealed that a clamping force of 5 in-lb was effective in securing the sample during testing without damaging the material (Figure 7).

![Graph](image)

Figure 7: Typical mechanical behavior of as-produced CNT sheet material used for wire fabrication.

**General Techniques**

In addition to these application-specific characterization techniques used to investigate the particular electrical and mechanical properties of bulk CNT materials, there are a few
common practices in CNT research. These methods focus primarily on estimating carbon nanotube size, morphology, quality, defect density and contamination.

Scanning electron microscopy (SEM) uses scattered electrons from the sample to create a highly magnified image of the surface morphology. SEM is often used to measure the approximate lengths of CNTs and to assess the degree of alignment and bundling in bulk samples. SEM is also useful in identifying the presence of contaminants (i.e. amorphous carbon particles, residual metal catalysts) within the sample through visual inspection (Figure 8). For this work, a Hitachi S-900 near-field emission microscope was used. The instrument was operated at an accelerating voltage of 2 kV and image magnifications ranged from 250 X – 100 kX.

Figure 8: Scanning electron micrographs of a KAuBr$_4$-doped densified CNT wire (bulk density≈1700 kg/m$^3$) cross section at 250X(left), 3.6kX (middle), and 25kX (right).

As an alternative to imaging contaminants using electron microscopy, the presence of non-CNT product can be characterized using thermal methods. Thermogravimetric analysis (TGA) is used to monitor the sample mass as it undergoes thermal decomposition in a
temperature-controlled oxidation. After the mass loss has stabilized (>800 °C; after CNTs and amorphous carbon have burned off), the remaining weight percent gives a quantitative analysis of the original non-carbonaceous sample content; typically the residual metal catalysts from synthesis (Figure 9). The TGA instrument used to determine metallic content for this work was a TA Instruments Model Q5000. Samples of ~1 mg were placed in a platinum pan and ramped at 10 °C/min from room temperature to ~1000 °C under flowing air at a rate of 90 cm³/min.

![Thermogram of CNT wire which was densified using deionized water as the lubricant, displaying approximately 10% by weight synthesis impurities in the as-produced material.](image)

Characterization of the quality and purity of carbon nanotubes is most commonly performed through the use of Raman spectroscopy. When monochromatic radiation is incident upon a sample, the light can interact with the sample in different ways. Depending on the energy of the incident light, it may be reflected, absorbed or scattered in some manner. For light
absorption to occur, the energy of the incident photon must be equal to the energy difference between two states of the molecule (the resonance condition). If this condition is met, the molecule can be found in an electronic excited state (if an ultraviolet, visible, or perhaps near-infrared photon was absorbed) or in a vibrational excited state (if an infrared photon was absorbed).

But, it is the radiation scattering, not absorption, which reveals information regarding the sample's molecular structure. When light is scattered from a molecule, most photons are elastically scattered. The elastically scattered photons have the same energy (frequency), as the incident photons. The dominant scattering process without a change of frequency is called Rayleigh scattering. However, a small fraction of light can be scattered by atoms or molecules at optical frequencies different from the frequency of the incident photons. The process leading to this inelastic scatter is termed the “Raman effect”. Raman scattering can occur with a change in vibrational, rotational, or electronic energy of a molecule. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule.

In quantum mechanical terms, the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The increased energy of this phonon mode will result in a corresponding loss of energy in the scattered light compared to the exciting photon. This 'Stokes scattering' is what is usually observed in Raman spectroscopy. In some cases, the molecules are initially in vibrationally-excited states. Raman scattering then results in the molecule descending to the ground state. This phenomenon of the scattered photon emerging at higher energy is called 'Anti-Stokes scattering'.
Specifically, for this experimental research, Raman spectroscopy surveys the symmetric vibrations of a carbon nanotube at a specified excitation wavelength (632 nm, determined by the laser used), which can be resonantly enhanced when using an energy corresponding to an absorption peak. The two most prominent peaks in the Raman spectra of CNTs are the disorder-induced D-band (occurring at ~1350 cm\(^{-1}\)) and the high energy mode G-band (occurring at ~1550 cm\(^{-1}\)). The G-band is present in all sp\(^2\)-bonded carbon materials and arises from in-plane vibrations in the lattice. The D-band is indicative of vacancies or impurities that create asymmetry in the lattice. The ratio between the G- and D-band intensities is often reported as a qualitative measure of CNT quality and purity, with high ratios representing a low defect concentration and high crystallinity in the sample.

In addition to these first order peaks, radial breathing mode peaks within the range of 100-300 cm\(^{-1}\) can be observed for samples containing SWCNTs. The location of these radial vibration modes correspond to the diameter for bundled SWCNTs, with peaks at lower Raman shifts corresponding to larger diameter SWCNTs.\(^{55}\)
Figure 10: Raman spectrums for a high density (HD) CNT wire lubricated with deionized water (top), low density (LD) CNT wire lubricated with deionized water (middle), and as-produced CNT sheet material (bottom).

For this work, Raman spectroscopy was performed using a JY-Horiba Labram spectrophotometer at room temperature using an excitation energy of 1.96 eV. Sample spectra were taken from 100-3000 cm\(^{-1}\).

**Results and Discussion**

**Densification/Solvent Interactions**

Whereas industrial metal wire drawing heavily relies on a vast market to provide combinations of water/oil-based and wet/dry lubricants,\(^{56}\) the previous work on CNT wire drawing was strictly water-assisted. Historically, the lubricant plays an important role in the wire
drawing process and is selected based on its ability to provide a smooth surface finish and to dissipate the heat produced from high speed drawing. In this work, lubricants were evaluated based on their ability to induce densification in the CNT wire, ease of removal from the system, effects on electrical conductivity, compatibility with potential additives, and friction reduction. Since the porous nature and high surface area of bulk CNT structures can promote adsorption, oil-based lubricants were avoided out of concern for difficulty arising in subsequent removal. Early successes in wire drawing lead to deionized water, N,N-dimethylacetamide, and acetonitrile being investigated in depth. Since deionized water was used as the lubricant in previous CNT wire drawing work, it was used once again in this work to serve as a baseline for other solvents used. Since CNT structures can display hydrophobicity, N,N-dimethylacetamide was used as a lubricant for its ability to interact favorably with CNTs. Lastly, acetonitrile was chosen for its inability to disperse CNTs, while being absorbed by the bulk CNT structure. Qualitatively, acetonitrile provided the best combination of friction reduction and smooth surface finish. Deionized water appeared to result in a rougher surface finish with occasional fraying along sections of the wire, but was used to produce the CNT wires with the highest degree of densification. The use of N,N-dimethylacetamide as a lubricant yielded smooth CNT wires, but caused a higher tendency of snagging during wire drawing, causing material losses during the process. Also, CNT wires subjected to N,N-dimethylacetamide would stretch significantly during the process, likely a direct result of the excellent CNT dispersion capabilities of the solvent. Electrical measurements revealed that acetonitrile and deionized water yielded wires with identical conductivities at equivalent densities, achieving a maximum conductivity of $2.5 \times 10^5$ S/m for a water-drawn CNT wire with a bulk density of $\sim 1500$ kg/m$^3$ (Figure 11). On the other
hand, N,N-dimethylacetamide produced wires with ~30% higher electrical conductivities than its equivalent density counterparts (Figure 12). This slight doping effect is perhaps caused by charge transfer resulting from the electron-donating character of the alkyl groups attached to the carbonyl of the amide.\textsuperscript{57}

Figure 11: Electrical conductivities of CNT densified wires drawn with acetonitrile and deionized water to various bulk densities.
Figure 12: Electrical conductivities of CNT densified wires drawn with N,N-dimethylacetamide and deionized water to various bulk densities.

The mechanical properties of any material are limited by the presence of defects in an otherwise perfect structure. In the case of high-performance CNT wires, these defects consist of topological defects (such as CNT entanglements which prevent perfect alignment and optimum packing), surface defects, and voids within the wire. Tensile testing was performed on a series of water-assisted drawn CNT wires at various densities to observe any mechanical/structural changes that arise from the drawing process (Figure 13). Upon further densification, the CNT wires exhibited less plastic extension as evidenced by the decrease in total strain from 40% to 10%. This resistance to deformation could be a consequence of a more entangled CNT network being formed during the drawing process and the creation of more stress points during tensile
loading. As expected, with the reduction of cross-sectional area under test, an increase in maximum stress was achieved from 90 MPa to 260 MPa. Despite this 300% increase, this maximum achieved value is still below the reported strength of cold drawn copper is slightly higher at 340 MPa. Since these samples were composed of roughly the same mass of material, the ultimate loads these samples were capable of withstanding were of interest to understanding changes imposed by wire drawing. On average, the breaking loads were consistently around an impressive 35 Newtons (3.5 kg) for a ~5 mg wire segment (Figure 13 bottom). From this data, it appears possible that once densities above 1000 kg/m$^3$ are reached, surface defects may be introduced, slightly compromising the load capacity of the CNT wires. As evidenced by the increased D/G ration upon densification (Figure 10), Raman spectrums also support this hypothesis.

In further pursuit of the ideal lubricant for CNT wire drawing, the mechanical strengths of CNT wires drawn with different lubricants were compared (Figure 14). Wires that had been drawn to equivalent densities with deionized water and acetonitrile exhibited very similar behavior. As mentioned previously, drawing CNT wires with the acetonitrile lubricant produced visually smoother wires. Mechanical testing supports this observation that of these two lubricants, acetonitrile might induce less surface defects or more effectively packed CNT networks, resulting in less deformation before failure and an increased elastic modulus. To fully confirm this hypothesis, further experiments, such as cross-sectional microscopy image analysis and surface roughness mapping of the CNT wires, would be beneficial.
Figure 13: Stress-strain curves for water-drawn CNT wires corresponding to bulk densities ranging from 500-1700 kg/m³ (top); corresponding ultimate loads for the water-drawn CNT wires as a function of their densities (bottom).
The comparable properties of these CNT wires drawn with water or acetonitrile as lubricants are promising. Having a variety of lubricants to choose from will provide significant flexibility in the types of organic or inorganic additives that can be integrated into the process to further enhance the performance of CNT wires.

**Carbon Nanotube Yarns**

In the wire industry, stranding and braiding of thin gauged wires into larger structures is implemented to create more flexible and mechanically robust wires, respectively. The replicate this method, the drawing die process was applied to thin CNT yarns acquired from Nanocomp Technologies, Inc (Figure 15). These yarns are spun in-situ from a CVD reactor, similar to the
The aforementioned Cambridge Method. The resulting yarns measure about 50 µm in diameter and can be continuously spun to lengths exceeding 1 kilometer. Raman spectroscopy reveals the presence of SWCNTs in the samples via the radial breathing modes, with a higher concentration of large diameters depicted by the strong peak at ~120 cm⁻¹ (Figure 16).

Figure 15: Scanning electron micrographs of commercial CNT yarn at 600X (top left), 1kX (top right), 5kX (bottom left), and 15 kX (bottom right).
In order to create a more robust wire out of CNT yarns, 60 individual strands were manually aligned and twisted with the aid of N,N-dimethylacetamide as a binder to create a cohesive cylinder. Once this cylinder was achieved, the drawing process was repeated in the same manner as for CNT sheets with N,N-dimethylacetamide as the lubricant to produce a bulk wire (Figure 17). Similar to the striations on the individual yarns, creases are visible on the surface of the wire resulting from the twisting applied to ensure the yarns would remain stranded and increase load transfer by increasing contact area.

![Raman spectrum of untreated CNT yarn; radial breathing modes highlighted in inset.](image)

Figure 16: Raman spectrum of untreated CNT yarn; radial breathing modes highlighted in inset.

The electrical conductivity of this densified CNT yarn wire was compared to the trend exhibited by the CNT sheet wire under the same drawing parameters (Figure 12). At equivalent densities, the wires composed of bulk CNT sheets electrically outperformed their yarn
counterparts by ~70% across the density regime investigated. It is possible that a higher resistance in the stranded wire was encountered due to restrictions in the conductive pathways for electrons created by the discrete yarns in the structure as opposed to having one continuous network of CNTs available for transmitting current.

Figure 17: Scanning electron micrograph of CNT wire composed of 60 CNT yarns.

The mechanical strength of a 1000 kg/m$^3$ stranded CNT wire was measured to evaluate any performance differences that could arise from the structural changes (Figure 19). When compared to bulk CNT wires of similar densities, the stranded yarn exceeded the maximum stress by approximately 10%, reaching 165 MPa before breaking. Improved mechanical strength is likely a result of an increased degree alignment of both CNTs within the yarn structure and alignment of the yarns within the wire, in addition to the aforementioned improved load transfer.
By exerting the pulling force in a direction parallel to the bulk alignment, the stranded wire is able to better distribute and withstand the load.

Figure 18: Electrical conductivity of densified CNT wire composed of CNT yarns at various bulk densities, compared to previously attained fit (Figure 12) for CNT sheet densification with N,N-dimethylacetamide lubrication.
Figure 19: Stress-strain curve for densified CNT wire composed of 60 individual CNT yarns (left); stitched image of CNT wire after mechanical testing (right).

A significant disadvantage in using commercial material is being restricted in terms of the underlying initial structure of the material. One often desirable goal is being able to reduce the amount of residual catalyst metal leftover from the synthesis. Through thermogravimetric analysis, it was measured that the noncarbonaceous impurities for a CNT yarn account for 12.9% of the total weight. Considering that these are likely iron oxide particles that only contribute mass to the finished product and do not aid in electrical conduction or mechanical strength, it would be beneficial to remove these components from the system without causing harm to the CNTs.
A common purification technique to remove catalysts from as-produced CNTs involves a high concentration acid reflux for an extended period of time. The chemical robustness of CNTs allows them to survive long term exposure to strongly oxidizing acids at high temperatures. When CNT sheets were subjected to acid reflux treatments, layers began to delaminate from the structure thus interfering with the drawing process. Therefore, subsequent purification treatments were tried on the more compact CNT yarns with varying degrees of success.

For all the different treatments, CNT yarn segments 15 cm in length were subjected to the solutions for 15 hours at 135°C. A standard acid reflux mixture of deionized water, nitric acid, and hydrochloric acid was delivered in a 10:5:2 by volume ratio as the first treatment (B) (Figure 20). For treatment C, the ratio of nitric acid to hydrochloric acid was reversed (10:2:5). In addition to acids, treatments D - G included varying concentrations of ethylenediaminetetraacetic acid (EDTA), an aminopolycarboxylic acid which has been widely used for its ability to sequester metal ions, in particular Fe$^{3+}$. After each treatment, the samples were briefly rinsed with deionized water.
In summation, substantial impurity removal was achieved with higher concentrations of hydrochloric acid with residuals accounting for 3.4% of the total yarn mass after treatment (Table 1). The addition of small amounts of EDTA to treatment mixture C appeared to inhibit the dissolution of the catalyst particles. It is possible that extended reflux periods could achieve equivalent or enhanced sequestering of the metal, but for these experiments treatment time was held constant. When increasing amounts of EDTA were added, an accelerated rate of impurity removal was observed, with final residual content measured at 3.1% after thermal oxidation up to 800°C.

Diameter reductions were reported for all the yarns that underwent purification treatments. Aside from being caused by the removal of noncarbonaceous impurities, the
solubility and subsequent removal of carboxylated carbons, which are a known decomposition product of nitric acid oxidation of carbonaceous material, could also account for the shrinking diameters.

Table 1: Summary of CNT yarn purification treatments and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>TGA Residue</th>
<th>Diameter [µm]</th>
<th>Load [N]</th>
<th>Stress [Mpa]</th>
<th>Strain [%]</th>
<th>Electrical Cond. [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>As-produced</td>
<td>12.9 %</td>
<td>53</td>
<td>0.83 ± 0.09</td>
<td>377 ± 40</td>
<td>15.1 ± 2.4</td>
<td>7.9 x 10^4</td>
</tr>
<tr>
<td>B</td>
<td>10:5:2, H_2O: HNO_3:HCl</td>
<td>10.1 %</td>
<td>44</td>
<td>0.38 ± 0.05</td>
<td>250 ± 35</td>
<td>3.0 ± 0.9</td>
<td>N/A</td>
</tr>
<tr>
<td>C</td>
<td>10:2:5</td>
<td>3.4 %</td>
<td>50</td>
<td>0.66 ± 0.12</td>
<td>348 ± 62</td>
<td>5.9 ± 1.3</td>
<td>N/A</td>
</tr>
<tr>
<td>D</td>
<td>10:5:2 + 12 mg EDTA</td>
<td>8.1 %</td>
<td>45</td>
<td>0.35 ± 0.11</td>
<td>225 ± 67</td>
<td>2.9 ± 0.9</td>
<td>N/A</td>
</tr>
<tr>
<td>E</td>
<td>10:2:5 + 18 mg EDTA</td>
<td>5.2 %</td>
<td>47</td>
<td>0.76 ± 0.08</td>
<td>473 ± 49</td>
<td>4.7 ± 0.9</td>
<td>N/A</td>
</tr>
<tr>
<td>F</td>
<td>10:2:5 + 31 mg EDTA</td>
<td>4.1 %</td>
<td>34</td>
<td>0.66 ± 0.06</td>
<td>768 ± 77</td>
<td>4.3 ± 0.6</td>
<td>N/A</td>
</tr>
<tr>
<td>G</td>
<td>10:2:5 + 51 mg EDTA</td>
<td>3.1 %</td>
<td>40</td>
<td>0.65 ± 0.04</td>
<td>603 ± 33</td>
<td>7.5 ± 0.3</td>
<td>2.0 x 10^5</td>
</tr>
</tbody>
</table>

*Mechanical properties are reported as averages calculated from 3-5 samples per treatment.

Another trend observed is the weakening of yarns treated with mixtures containing higher concentrations of nitric acid (B & D), with fracture occurring after an average load of 0.37 N. For comparison, untreated yarns withstood loads averaging 0.83 N and yarns treated with higher concentrations of hydrochloric acid broke after loading 0.68 N. From the tests in which the amount if EDTA was varied, it is evident that EDTA is not contributing to the loss of strength. Taking into account the ensuing diameter reductions, EDTA-containing treatments E-F actually result in higher mechanical strengths (Figure 21). This promising result is potentially due to the removal of “inactive” material which does not contribute to the mechanical performance of the yarns, leaving behind a tighter and stronger network of CNTs.
Lastly, the electrical conductivities of as-produced and treatment \( G \) yarns were measured to determine whether the acidic treatments caused any adverse effects to the CNT conductive networks. In fact, both the electrical conductivity and resistance per unit length (57.2 \( \Omega/cm \) pre-treatment and 48.0 \( \Omega/cm \) post-treatment) improved. This increase in electrical conductivity is attributed to charge-transfer doping by the acid treatment resulting in p-type doped CNTs.\(^6\)

**Doping Effects**

Tailoring the electronic properties of carbon nanotubes can be a central point for many applications ranging from nanoscale transistors to bulk structures, as is the case in this body of work. When working with CNTs, there are three primary doping strategies: endohedral doping,
in-plane doping, and exohedral doping. Endohedral doping relies on the intercalation of structures within the CNTs. In-plane doping involves the substitution of carbon atoms along the lattice by other atoms, resulting in p-type or n-type semiconductors depending on the atoms chosen. In the case of exohedral doping, organic and inorganic molecules can be chemically adsorbed or physically absorbed onto the CNT surface. Exohedral doping represents the most robust and versatile method for doping CNTs and was thus pursued further in this work.

Despite the extensive amount of research on the chemical doping of CNTs, the underlying doping mechanisms are still argued. Recently, a new strategy has been proposed for controlling the doping types by selecting possible dopants based upon their reduction potential, relative to that of CNTs. A chemical with a higher reduction potential than that of a CNT is referred to as an acceptor for its tendency to extract electrons from the CNT. Conversely, a chemical with a lower reduction potential is considered a donor for its ability to give electrons to the CNT. Electron-accepting adsorbates can be used to downshift the Fermi level toward the valence bands of CNTs, resulting in p-type doping.

Doping of CNTs by salt solutions such as HAuCl₄, Na₂PtCl₄, K₂PdCl₄, and NOBF₄ appear to have different reaction mechanisms compared to direct adsorption of organic molecules. It has been proposed that a redox reaction occurs due to the higher reduction potentials of the cations in solution, resulting in p-type doped CNTs. The charge transfer reduces positive ions such as Au³⁺, Pt²⁺, Pd²⁺, and NO⁺ to metal particles or gas and results in p-type doped CNTs. Since CNTs possess a reduction potential of about +0.5 V vs. SHE (standard hydrogen electrode), the reduction of Au³⁺ (AuCl₄⁻/Au, +1.002 V vs. SHE), Pt²⁺ (PtCl₄²⁻/Pt, +0.755 V vs. SHE), and Pd²⁺ (PdCl₄²⁻/Pd, +0.591 V vs. SHE) into metal nanoparticles through a galvanic displacement reaction can occur without the aid of a reducing agent.
Based on studies involving CNT thin films, the remarkable reduction in sheet resistance in the case of Au\(^{3+}\) ions is also observed in the case of NO\(^+\) ions.\(^{62}\) This suggests that the gold nanoparticles that spontaneously form on the surfaces of CNTs do not aid in electron transport. Experiments conducted with various Au\(^{3+}\) ionic salts during this work support this theory. In this present work, when CNT papers were submerged into aqueous solutions of KAuCl\(_4\) and KAuBr\(_4\), roughly the same electrical conductivity was measured for all the samples, yet significant gold plating only occurred with the KAuCl\(_4\) samples. Since it was determined that the gold plating was unessential for high electrical conductivity, the appeal of mass savings resulted in further investigation into the performance of KAuBr\(_4\)-doped CNTs.

Whereas gold chloride salts have been commonly used for CNT doping,\(^{62-65}\) the effects of KAuBr\(_4\) doping have not yet received much attention. With a slightly lower reduction potential of 0.854 V vs. SHE for AuBr\(_4^-\)/Au,\(^{66}\) the rate and magnitude of adsorption of Au particles onto the CNT surface should be diminished, thus reducing the weight of the CNT structures while maintaining the high electrical conductivity.
In the present work, the prospect to increase the bulk electrical conductivity through concomitant densification of CNT sheets in the presence of a chemical dopant has been pursued. An aqueous solution of KAuBr$_4$ was selected as a doping agent and incorporated during the wire fabrication process as a lubricant at a 2 mg/ml concentration. Based on previous work in which the CNT conductance rapidly rises to a plateau in 40 seconds after exposure to HAuCl$_4$ (the time attributed to the nucleation stage of metal nanoparticles on the CNTs), the CNTs in this work were exposed to the KAuBr$_4$ doping solution for 5-30 minutes. An extended soak time was implemented to ensure diffusion through the material. Figure 22 shows that the CNT wires exposed to the KAuBr$_4$ solution display five-fold increases in electrical conductivity over their undoped counterparts. Furthermore, an order of magnitude increase is observed when doping is...
used in concert with densification to reach a bulk electrical conductivity of $1.3 \times 10^6$ S/m for a CNT wire; this value exceeds any electrical conductivity reported of bulk CNT materials to date. Raman spectroscopy on the densified and doped CNT wires did not show any discernible features in typical resonance Raman features, indicating that the structural integrity of the CNTs is maintained during densification (Figure 23). The marginal increase in bulk density for the highest conductivity CNT wire is attributed to the dopant mass. TGA data showed that CNT sheet incubation in KAuBr$_4$ for several minutes led to a 2-3% weight increase in noncarbonaceous residue, suggesting a small amount of reaction products were deposited on the material (Figure 24).

![Image of Raman spectrums](image_url)

**Figure 23:** Raman spectrums for a KAuBr$_4$ doped HD CNT wire, KAuBr$_4$ doped LD CNT wire, undoped HD CNT wire, undoped LD CNT wire, and as-produced CNT sheet (from top to bottom on plot).
As an alternative to doping with inorganic salts, chemical doping of CNTs via organic molecules was also investigated. Tetracyano-p-quinodimethane (TCNQ) is a very well-known electron-acceptor molecule, which has been successfully used for the preparation of electrically conducting salts and charge-transfer complexes to induce p-type doping by encapsulating CNTs.\textsuperscript{67} The appeal of this particular organic molecule stems from its non-hygroscopic nature and also flexibility in modifying the molecule for future investigations.

For this work, solutions of 7,7,8,8-Tetracyanoquinodimethane in acetonitrile were made at a concentration of 4 mg/mL and used as a lubricant for the CNT wire drawing process. Although the TCNQ solution results in a ~65% increase in electrical conductivity over strictly
acetonitrile (Figure 25), the KAuBr$_4$ solution still represents an over 100% increase over the organic dopant.

Figure 25: Electrical conductivity of densified CNT wire doped with TCNQ at various bulk densities, compared to previously attained fit for CNT sheet densification with acetonitrile lubrication (left); chemical structure of TCNQ (right).

Figure 26: Images depicting temperature dependent electrical conductivity experimental set-up with CNT wire segment in contact with probe tips while mounted on Al$_2$O$_3$ plate.
Figure 27: Temperature-dependent electrical conductivity for representative samples of doped and undoped CNT wires at different levels of densification (uncertainty in measured values is within the data points), with modeled curve fits superimposed with data points.

Temperature dependence of the electrical conductivity has been used to interrogate the nature of the dominant conduction mechanisms in bulk CNT materials. Four-point probe conductivity was measured in situ as a function of temperature on representative samples with a Janis Research Co. LN$_2$ cryostat over the temperature range of 100-400 K after sample equilibration under high vacuum ($< 10^{-6}$ torr) in excess of 36 hours (Figure 26). Figure 27 depicts the temperature-dependent conductivity data for a water-drawn low density (LD) CNT wire, a
water-drawn high density (HD) CNT wire, a KAuBr$_4$ doped LD CNT wire, and a KAuBr$_4$ doped HD CNT wire. Throughout the temperature range investigated, a steady increase in conduction is observed with increasing temperature for the water-drawn CNT wires; commonly attributed to fluctuation assisted tunneling between adjacent CNTs.\textsuperscript{68,69} Conversely, the temperature profile for the KAuBr$_4$-doped CNT wires exhibit conventional metallic behavior in which the electrical conductivity decreases with increasing temperature.

Previous work has successfully curve fit the CNT temperature-dependent conductivity data using a functional form which represents the temperature-induced voltage fluctuation-assisted tunneling between metallic regions, highly anisotropic metallic conduction, and the variable-range hopping in disordered semiconductors, which are the primary conduction mechanisms prevalent in these materials.\textsuperscript{70} The resulting functional form is as follows:

$$ \sigma(T) = A \exp\left(-\frac{T_m}{T}\right) + B \exp\left(\frac{T_b}{T_s + T}\right)^{-1} + H \exp\left(-\left(\frac{T_0}{T}\right)^\gamma\right) $$

(5)

The coefficients A, B, and H depend on the resistivity of the CNT networks arising from the morphology, primarily, the alignment and density. These values are used to determine the relative contribution to the overall electrical conductivity of the metallic regions along a carbon chain, the resistance associated with fluctuation-assisted tunneling through thin barriers, and variable range hopping, respectively (Figure 28).\textsuperscript{68} The fitting parameter, $T_b$, is related to the magnitude of the tunneling energy barrier, while $T_s$ denotes the turning point temperature at which thermally activated electrical conduction over the barrier will occur. The metallic parameter, $T_m$, is linked to the energy of backscattering zone boundary phonons for the carbon nanotubes. The variable range hopping term was deemed negligible over this temperature range and omitted from the modeled curve fits to focus on the dominant conduction mechanisms.
Figure 28: Illustration depicting the significance of conduction mechanism coefficients A and B.

Table 2 highlights the differences in $T_s$ and $T_m$ between doped and undoped CNT wires which indicate that doping with KAuBr$_4$ lowers both the temperature at which fluctuation-assisted tunneling becomes significant and the metallic parameter for the undoped CNT wire. Since densification was not expected to alter conduction along the individual CNTs and the shape of the data was constant with densification, the values for $T_s$ and $T_m$ were assumed to be unaffected by densification. The magnitude of the tunneling barrier between CNTs in the wire is also shown to systematically decrease with doping and increased densification. The forced proximity of adjacent CNTs, from densification, slightly lowers the tunneling barrier energy for both undoped and doped CNT wires. As expected, the coefficients A and B decrease with doping and densification, representing the increase in absolute conductivity following the treatments.

Table 2: Conduction Mechanism Modeling Parameters.

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<tr>
<td>LD H$_2$O</td>
<td>8.01</td>
<td>4.01</td>
<td>133</td>
<td>166</td>
<td>377</td>
<td>32.4</td>
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<tr>
<td>HD H$_2$O</td>
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<td>2.51</td>
<td>133</td>
<td>166</td>
<td>276</td>
<td>23.8</td>
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<td>2.00</td>
<td>226</td>
<td>93</td>
<td>104</td>
<td>9.0</td>
</tr>
<tr>
<td>HD KAuBr$_4$</td>
<td>0.96</td>
<td>0.49</td>
<td>226</td>
<td>93</td>
<td>90</td>
<td>7.8</td>
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The stability of the densification and doping process under high vacuum ($10^{-6}$ torr) was monitored under illumination from a UV light source (200W Hg-Xe bulb) and variable temperature for 16 hours. Both the H$_2$O densified and the KAuBr$_4$ doped CNT wires did not exhibit any detectable changes in resistance with either thermal fluctuations (between 150 K and 325 K) or illumination.

In conclusion, the ability to simultaneously densify and dope as-synthesized CNT sheets represents a novel approach to achieve high electrical conductivities in bulk wire structures. The extent of densification and doping, in concert, is shown to significantly influence the tunneling barrier for electron conduction between adjacent CNTs.

Another type of doping which was investigated focused on the conductivity of electronic-type pure SWCNTs. Previous theoretical simulations have shown that electron transport depends strongly on the intermolecular junctions formed between carbon nanotubes, more specifically that conductance can be an order of magnitude smaller for mixed junctions between metallic and semiconducting SWCNTs. Recent advances in phase separating SWCNTs, through a series of density gradient ultracentrifugations of surfactant-stabilized SWCNTs dispersions, have resulted in NanoIntegris Inc. providing the first commercially available phase-pure SWCNTs in bulk quantities. Buckypapers comprised of 99% semiconducting SWCNTs and 98% metallic SWCNTs were purchased, and a 7 mm x 7 mm square was used for temperature dependent electrical conductivity measurements to probe the nature of conduction in electronic-type pure SWCNT bulk samples. Before recording data, the samples were allowed to equilibrate under vacuum ($< 10^{-6}$ Torr) and were cycled through the full temperature range of interest (77 - 400 K) to promote desorption of any unwanted species in the samples. Uncertainty in the electrical
conductivity arises from the average of 3 current-voltage sweeps and instrument limitations in measuring the sample dimensions.

Slight differences at room temperature were observed, with the metallic sample measuring $2.1 \times 10^4$ S/m and the semiconducting sample measuring $1.7 \times 10^4$ S/m (Figure 29). Whereas the semiconducting sample exhibits conventional thermal behavior of decreasing resistance with increasing temperature, the metallic sample also displays this trend. This feature and also the low magnitudes of these values leads one to predict that electron conduction is being severely limited in these samples. The same features of surfactants that allow them to wrap SWCNTs and create stable dispersions, also makes them difficult to completely remove. These low electrical conductivities are likely caused by residual surfactant chains interfering with the tunneling or hopping of electrons between SWCNTs.

Figure 29: Temperature-dependent electrical conductivity for electronic-type pure SWCNTs.
Contacting

In order to implement a new technology, application-specific issues need to be addressed. One such issue encountered during this research was limited options in connecting the CNT wires to other electrical components. In microelectronic devices, a focused electron beam in conjunction with a highly conducting solder is commonly used to attach individual CNTs to metal electrodes.\textsuperscript{73} The scale, economics, and practicality of this method present obvious conflicts in adaptation for bulk CNT wires.

A conventional metal solder (tin-lead composite) was applied to bulk CNT wires and sheets, but was unable to wet the CNT surface and form a reliable electrical contact with a tab of pure copper foil (Figure 30). It was later shown that gold plating via thermal deposition onto the CNT sheet can enhance wettability, but with a relatively high cost of time, materials, and equipment.

Figure 30: Image depicting the inability of solder to wet the CNT sheets.

As an alternative joining technique, ultrasonic welding is a versatile process with extensive applications in both the metals and plastics industries. Ultrasonic welding has been used to join dissimilar materials by applying the energy from high frequency vibrations onto the
interface area between the parts to be welded. The materials are pressed together between the ultrasonic horn and stationary anvil at a user-specified pressure. Once the workpieces are clamped, the horn oscillates at a resonant frequency, which is determined by the transducer component of the system. The amplitude of vibration on the front end of the transducer is typically in the range of 5 - 30 µm. The surfaces of the horn and anvil also feature interchangeable knurl patterns to better grip the materials.

When welding thermoplastics, the absorption of vibrational energy (which is applied perpendicular to the weld interface) creates localized heat causing the materials to plasticize locally before welding together. Since carbon nanotubes remain stable up to very high temperatures, close to the melting point of graphite near 4000 K, a different mechanism should be responsible for ultrasonic welding of CNTs.\textsuperscript{61}

When welding metals, the friction-like relative motion between the two surfaces serves to deform, shear, and flatten local surface roughness, scrubbing away interfacial oxides and contaminants to establish increased contact area and bonding between the materials.\textsuperscript{74} Although heat is generated in ultrasonic welding of metals, this process occurs in the solid state with no melting or fusion taking place.\textsuperscript{75}

Recently, the application of ultrasonic welding technology has resulted in the formation of mechanically reliable bonds between SWCNTs and titanium and gold electrodes.\textsuperscript{76} In addition, the improved stability and low-Ohmic contact of the weld enhanced the performance of the field-effect transistors fabricated. After welding, it was observed that the ends of the individual SWCNTs that overlapped the metal were now embedded into the surface and barely
visible. As a proof-of-concept, this process was briefly investigated for bulk SWCNTs with a weld area of 50 µm².

From these findings, an underlying mechanism for ultrasonic nanowelding was proposed in which high-frequency ultrasonic energy induces plastic deformation of the metal under the clamping pressure because of the “acoustic softening effect”zs. Studies on the effects of ultrasound on the deformation characteristics of metals further support this notion, reporting that the Young’s modulus of many metals (including copper, aluminum and gold) is reduced substantially when acoustic energy is applied during tensile testing. This ultrasonic deformation allows the nanoscale materials to be embedded into the metal electrodes.

This process is highly favorable for space applications considering that no additional components are added to form the bond. This is considered beneficial since any bond-enhancing material would not only add mass to the craft, but would also need to meet the strict regulations concerning outgassing and thermal performance to be approved for space use.

For this work, an AmTech Ultraweld-40 system was used for bonding doped CNT wires to copper metal foils (Figure 31). This welding system is designed to operate at a tuned frequency of 40 kHz. The topic of critical frequencies for optimum welding has been discussed from a fundamental metallurgical physics perspective (e.g. exciting dislocation fields), but there has been no evidence of such material behavior in the conventional frequency range of ultrasonic welding (15 – 300 kHz). The welding process was carried out at room temperature for a duration of 0.1 – 1.0 seconds, which is much shorter than conventional contacting techniques. All welding was performed on a 3.5 mm x 3.5 mm contact area to 35 µm thick copper foil with an unpatterned welding tip and a knurled anvil to better grip the metal foil. Mechanical testing
was performed on a TA Instruments Dynamic Mechanical Analyzer Q800 with a force ramp rate of 0.5 Newtons/minute. Since the weld area was constant for all the samples investigated, mechanical results were reported in terms of grams with a sample set size of 4-6 bonds per treatment (error bars on plots represent the standard deviation within these sets).

![AmTech Ultraweld-40 ultrasonic welder](image1.png)

Figure 31: Image of AmTech Ultraweld-40 ultrasonic welder used for welding CNT wires to metal foils (left); schematic of welding process (right).

In this welding system, vibration amplitude is an independent variable set by the user, with a maximum attainable value of 18 µm. As a result of various trials, it was determined that vibration amplitude of the welding tip is one of the key parameters affecting weld quality (Figure 32). By increasing the vibration amplitude from 12 to 18 µm, it is proposed that the level of plastic deformation and shearing that occurs is increased. This allows more CNTs to be embedded into the base metal, therefore creating a stronger bond between the materials, with maximum weld loads exceeding 1 kg on several samples.
The magnitude of the clamping force introduced perpendicular to the welding interface can also be a key parameter of ultrasonic welding. Prior to clamping, the two materials are only in contact at intermittent areas determined by surface roughness. In theory, an increase in clamping force should increase the contact area up to a certain threshold. Ultrasonic vibrations are then responsible for extended contact areas and weld formation. The magnitude of the force required will be strongly dependent on the hardnnesses and thicknesses of the materials being welded.\textsuperscript{75} Since the clamping force is also determined by the size of the weld being produced, often pressure is the metric used during operation to normalize for different weld areas. Through adjusting system parameters, an optimum range of pressures is sought, below which welds will be weak or non-existent and above which excessive deformation of the specimens may occur. For the combination of vibration amplitudes and weld energies investigated, the clamping pressure was varied between 20, 40, and 60 psi. The pressure of 20 psi did not consistently yield welds capable of testing. When the welding pressure was increased from 40 psi to 60 psi, the average maximum load slightly increased by approximately 40 grams. Based on the maximum load deviation within the sample sets, it remains unclear which of these pressures is preferable. In light of these results, higher pressures were investigated but the copper foil tabs (at this thickness) began to lose their structural integrity.
Figure 32: Summary of parameter optimization study for ultrasonic welding CNT wires to copper foils.

Energy, power, and time are treated as coupled welding parameters. When a weld is made, the voltage and current result in a time-varying flow of electric power to the transducer. A simple, representative power curve (Figure 33) will have a peak power and weld time. For this work, the weld energy (electrical energy supplied to the transducer represented by the area under
the power curve) was varied so that the weld would run until the set level is achieved. In this work, the mechanical integrity of welds produced using four different weld energies were investigated (40, 80, 120, 160 Joules). Welds made with 80 Joules of electrical energy produced the most consistent results and the highest average maximum load. It is likely that a time threshold can be reached where extended weld periods have a negligible effect, and perhaps begin to induce damage in the materials.

Figure 33: Schematic of an ultrasonic welder’s representative power curve.

Compiling the results of these investigations into optimum ultrasonic weld parameters for doped CNT wire to copper foil contacts, yielded samples with average maximum loads in excess of 1 kg (Figure 34). The feasibility of ultrasonic welding to other highly conductive metal foils was briefly investigated by applying the same optimized welding parameters from the copper foil experiments to silver foil. Successful welds were made between the CNT wires and the silver
foils with \(~15\%\) decrease in maximum load capabilities, likely arising from difference in material hardness and modulus.

Figure 34: Mechanical performance of optimized weld between CNT wire and copper foil; vibration amplitude = 18 \(\mu\)m, weld pressure = 60 psi, and weld energy = 80 J.

Mechanical performance of CNT wires bonded to metal foils after thermal shock cycling between 160°C and -200°C (10 complete cycles with 1 minute soak time in oven and liquid nitrogen bath, respectively) was examined. Independent of the metal foil used, the maximum load the ultrasonic welds could withstand dropped to approximately 300 grams after thermal cycling (Figure 35). In an attempt to decouple the effects from the thermal shock, the testing was also performed on a sample set that endured a temperature cycle of 20°C – 160°C and another sample set that experienced a temperature cycle of -200°C – 20°C. It was determined that the weld suffers in both situations, but is better suited to withstand warmer temperatures.
In addition to high mechanical endurance, CNT wire welds can benefit from low electrical contact resistance. Contact resistance is a commonly encountered issue in semiconductor devices, where the contacts are generally between a metal and a semiconductor. The contact resistances arise from energy band barrier heights formed by the difference between the work function of the metal and the electron affinity of the semiconductor. The work function of a solid is defined as the energy difference between the vacuum level and the Fermi level. The electron affinity of the semiconductor is defined as the potential difference between the
conduction band and the vacuum level. The vacuum level represents the energy of a free electron in vacuum and is often used as a reference level when comparing band diagrams of different materials. The difference between the work function of the metal and the electron affinity of the semiconductor can be expected to cause the transfer of electrons from the semiconductor into the metal, resulting in an abrupt discontinuity of allowed energy states at the interface.\textsuperscript{80}

Figure 36: Illustration of conventional transfer length method for calculating the contact resistance between a metal and a semiconductor surface.

Considering the resistance between points A and B having two separate metallic conductors lying on the surface of the bulk CNT materials (Figure 36), the total resistance $R_{Total}$ is represented by Equation 5; its three components: (1) the resistance of the metallic conductor $R_M$, (2) the contact resistance $R_C$ between the metal and CNTs, and (3) the bulk CNT resistance...
$R_{TN}$, where $N$ is being used to annotate electrical resistances corresponding to different lengths of bulk CNT material.

$$R_{Total} = 2R_M + 2R_C + R_{TN}$$ (6)

In this work, a lateral four-contact, two-terminal contact resistance structure was devised to make relative comparisons between CNT-copper bonded samples fabricated using different welding parameters (Figure 37). The modified transfer length method (TLM) was modeled after conventional semiconductor characterization techniques. In this modified TLM test structure, two separate, ultrasonically bonded copper foil tabs at the ends of a CNT wire served as the source and drain for the current. One of the tabs extends towards the opposite end, leaving a small separation from the other copper tab. Initially, a freestanding polyimide film is placed between the CNT wire surface and the non-bonded copper foil extension to prevent electrical contact. The voltage drop across the structure was measured and used to calculate the total resistance across the tab separation length. Following the same process, successive ultrasonic bonds were made between the copper tab extension and the underlying CNT wire resembling a “ladder” structure. The measured total resistances between adjacent, discrete contacts were plotted as a function of tab spacing from which the contact resistance between the copper foil and CNTs can be extrapolated (Figure 38).
Figure 37: Modified structure for relative comparisons of contact resistances between ultrasonically welded CNT wires and metal foils.

Figure 38: Schematic of typical method of experimentally determining the contact resistance and transfer length between metal and semiconducting surfaces.

In the interest of time, only certain welding parameters which yielded mechanically robust CNT-copper bonds were investigated electrically. Specific contact resistivity ($\rho_c$ [Ω-cm²])
was used to characterize these contacts because it is normalized to contact area. For each weld, the contact area was measured as 5.4 mm x 1.6 mm, or 0.0864 cm².

Once the optimized weld parameters were determined (18 μm, 60 psi, 80 J), confirmation was sought on the idea that a more mechanically robust weld would yield a more conductive weld. For this experiment, two identical KAuBr₄-doped CNT wires were welded to copper foils following the modified TLM structure detailed previously. The weld pressure (60 psi) and weld energy (80 J) were held constant when welding both wires, but the vibrational amplitudes were varied to produce a strong weld (18 μm) and a weaker weld (12 μm). When electrical measurements were performed (Figure 39), a specific contact resistance of ~0.0176 Ω·cm² was calculated for the weaker weld and ~0.0043 Ω·cm² for the stronger weld, confirming the theory that better mechanically-performing welds would also promote electron transport.

Furthermore, the effects of CNT doping on the specific contact resistance of CNT wires ultrasonically welded to copper foils were investigated under the same optimized welding parameters. Comparing with the KAuBr₄-doped CNT wire specific contact resistance reported above, an undoped (water-drawn) CNT wire encounters a specific contact resistance over twice as high at ~0.0099 Ω·cm² (Figure 40). This suggests that chemical doping can not only reduce the resistance of the wire itself, but also the contact resistance between the wire and other materials.
Figure 39: Total resistance as a function of probe separation for two ultrasonically welded copper foil and KAuBr₄-doped CNT wire systems (uncertainty in measured values is within the data points); used to evaluate specific contact resistance changes with welding parameters.
Figure 40: Total resistance as a function of probe separation for two ultrasonically welded copper foil and CNT wire systems (uncertainty in measured values is within the data points); used to evaluate specific contact resistance changes with CNT doping.

The mechanical and electrical results from ultrasonically welding CNT wires to metal foils were comparable to other experiments involving contacting to metals via mechanical crimping and commercial conductive silver epoxies.

**Technology Demonstrations**

In order to demonstrate the data and power transmission capabilities of CNT wires, a functional USB cable was constructed (Figure 41). In total, four CNT wires measuring ~50 cm in
length were insulated with polyolefin heat shrink tubing. One set of wires is used to transmit a voltage of ~5 V, and a twisted pair was used to carry the data.

Without proper testing equipment, a test bed of a timed file transfer was implemented to compare a conventional USB cable and the CNT cable. Successful transfer of a 4 gigabyte file occurred at the speed over both cables, with a differential of about +1 seconds (~0.5% of the total time required) for the CNT wire file transfer.

Figure 41: Image depicting carbon nanotube USB cable construction.

The Smith chart is used to graphically represent the complex reflection coefficient and the complex impedance for single-port microwave components. Nonzero reflection coefficients arise when a propagating wave encounters an impedance mismatch. In a Smith chart, the
segments lying in the top half on the complex-impedance represent inductive reactances, and those lying in the bottom half represent capacitive reactances.

To evaluate the use of both CNTs as the inner conductor and electromagnetic shielding, three test wires were constructed by hand and tested for their impedance as a function of frequency (Figure 42). The first sample consisted of a commercial RG-58 cable that had been disassembled and then reassembled to act as a control (“Steel Shield”). The second cable was constructed from all the same materials, but with a doped CNT wire acting as the center conductor (“CNT center”). The third cable was designed to evaluate the shielding effectiveness of CNT sheets by replacing the steel shielding in the cable with a copper conductor (“CNT Shield”).
Figure 42: Smith charts for conventional RG-58 control copper cable (top left), RG-58 cable with CNT wire center conductor (top right), RG-58 cable with CNT shielding (bottom left); image of experimental set-up with wire under test (bottom right).

It is very promising that the Smith charts for all the samples are very similar, with the two CNT samples featuring slightly smaller reflection coefficients and significant weight savings. But it is difficult to conclude that CNTs outperformed conventional materials when it is likely that manual construction of these cables might be the dominant factor in determining their properties. High-end RF cables are manufactured to very high tolerances with specialty equipment; this same treatment would be necessary with CNT wires and shielding to better determine their full potential in the RF industry.
Appendix A: Image Processing

Image processing software package *ImageJ* was used to analyze the void spaces in a scanning electron micrograph of a high density CNT wire cross section (Figure 43). Unfortunately, the process used for cutting the CNT wire to expose a flat surface also induces slight deformation in the sample. With these results, an approximate minimum void volume of 12% remains after the drawing process.

![Figure 43](image)

**Figure 43:** Image processing results of the cross sectional area of a high density CNT wire.
Current work is continuing the investigation of void spaces in these bulk CNT wires. The use of focused ion beam technology will allow the areal density uniformity throughout the entire wire to be analyzed, without deforming the wire through manual cutting.

Appendix B: Thermal Expansion

The ability of a material to maintain physical stability in strenuous environments is also essential to its success for both Earth and space structures. Most metals undergo thermal expansion, an effect attributed to the anharmonicity of the interatomic potential.\textsuperscript{81} For carbon nanotubes, molecular dynamics simulations conclude that at moderate temperatures (T < 1000 K), the gain in entropy translates into longitudinal contraction.\textsuperscript{82}

A simple experiment was conducted on the TA Instrument DMA to investigate whether this phenomenon occurs in bulk CNT structures. The length of the sample was monitored as it underwent sequential thermal cycles of 30 – 300 °C performed while the sample was under a constant load of 0.05 N (Figure 44).

For the temperature range investigated, the drawing process did not affect the contraction behavior as the length of both the CNT sheet and CNT wire contracted by 0.75%. For a solid, the fractional change in length per degree of temperature change can be calculated using the following equation

\[
\frac{\Delta L}{L} = \alpha_L \cdot \Delta T
\]

(7)
where \( \alpha_L \) represents the coefficient of thermal expansion for the solid; 0.000017 /°C in the case of copper. For comparison, over the same temperature range, a copper structure is expected to expand 0.45%.

Figure 44: Thermal contraction behavior of CNT sheet and wire in the temperature range 30-300 °C compared to theoretical model for copper.

Conclusions

The focus of this work was to successfully draw commercial carbon nanotube sheets into durable, high density wires and investigate their potential as alternatives to conventional wiring for aerospace applications. Mechanical and electrical measurements were performed on initial wires fabricated following a procedure previously established in literature to serve as a baseline; these values both fell short of the reported properties of copper. The electrical conductivity was
enhanced by introducing N,N-dimethylacetamide as a lubricant during the drawing procedure, but also resulted in material loss. The mechanical strength of the CNT wires was improved by using acetonitrile to assist the densification process. Bulk densities were reported and used to accurately compare values across the many samples created throughout this work with little deviation. Simultaneous densification and chemical doping with an ionic KAuBr₄ solution yielded a CNT wire which exhibited an electrical conductivity of 1.3 x 10⁶ S/m, almost twice as high as the previously reported maximum electrical conductivity for a bulk CNT structure. Although further improvements in the electrical conductivity of CNT wires is still required to surpass the conductivity of copper, the combination of radiation tolerance, oxidation resistance, and flexure endurance of CNT materials will continue to push their advancement as viable next-generation wiring alternatives.

A method of contacting CNT wires to metallic surfaces was developed through ultrasonic welding. In addition to parameter optimization for mechanical strength, an electrical measurement technique allowing relative comparisons of contact resistances was introduced, determining that mechanically robust bonds yield lower contact resistances and that chemical doping can also reduce the contact resistance between CNTs and copper.
References

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