2011-01-01

Experimental Study Of Thermoelectric Properties For Randomly Distributed Carbon Nanotubes And Silicon Carbide Nanoparticles

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EXPERIMENTAL STUDY OF THERMOELECTRIC PROPERTIES
FOR RANDOMLY DISTRIBUTED CARBON NANOTUBES
AND SILICON CARBIDE NANOPARTICLES

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Dedication

This thesis is dedicated to my family who has provided me with unconditional support and motivation. May this thesis symbolize my gratitude, and my promise to give back to them and my community.

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by

Onasis Garcia, B.S. Mechanical Engineering

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

Department of Mechanical Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

December 2011

Acknowledgements

I would like acknowledge first and foremost my advisor Dr. Khan for giving me the opportunity to research as his graduate student, and thank him for his dedication, guidance, and composure at all times. I would also like to give special thanks to Dr. Choudhuri for finding and allocating a research opportunity, and for his resourcing support to pursue it.

I would also like to acknowledge all the employees from the Center for Space Exploration and Technology Research (cSETR). These employees include but are not limited to; Adrian Trejo, Vishwhanath Ardha, Bidhan Dam, Satya Kiran, Mark Flores D. Flores, and Ashvin Kumar. Throughout the entire experimentation phase of my research, I run into several complications that I would have not resolved otherwise if it wasn't for the support and expertise of the people just mentioned. I would also like to thank the cSETR associate director Nathaniel Robinson, and the cSETR/Mechanical Engineering administration staff.

Lastly, I would like to acknowledge my committee members for their kindness of accepting to be part of my evaluating committee, and for the professional recommendations that they can provide.

Abstract

In this experimental study, the thermoelectric (TE) properties of carbon nanotubes (CNTs) and Silicon carbide (SiC) nanoparticles have been investigated. Nanoparticles were randomly disrtibuted on a non-conductive glass or quartz substrate. The carbon nanotubes used were single-walled and multi-walled type, consisting of approximately 60% semiconducting 40% metallic tubes. The experimental design is analogous to that of a thermocouple measurement, with the nanoparticle layers creating hot and cold joints with a dissimilar metal Alumel (Ni-Al). Voltage (mV), current (μA) and resistance (Ω) values were measured with respect to temperature (°C), and Seeback coefficient values were also calculated in parallel. Summarized results demonstrate SWNTs offer an overall thermoelectric advantage, approximately double in magnitude for voltage, current, and Seebeck coefficient results. Furthermore, isolated SiC nanoparticles demonstrate no TE effect. However, SiC introduce distinctive thermoelectric effects on CNTs dependant on the type of CNTs and the method SiC is introduced (e.g. as a layer vs a compound mixture). Doping of CNTs was also examined and discussed to similarly identify the thermoelectric properties and semiconducting characteristics accordingly.

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Chapter 1.0: Introduction

1.1 Project Overview

Demand for innovation in the advancement and/or development of novel sensor-like materials with superior mechanical, electrical, and thermal properties at high temperature condition has lead to a need for further experimentation and new technologies in this field. For instance, the Department of Energy targeted the need for advances in sensor materials and novel approaches to monitor thermal conditions for applications of energy conversion processes (e.g. gasification, oxygen fired combustion, hydrogen rich combustion turbines, etc). Under these conditions traditional instrumentation and sensors fail to perform adequately [1].

Current Era Innovation is exploiting advances at the nano-scales (e.g. nanomaterials). In view of that, carbon nanotubes (CNTs) have gained substantial recognition because they have revealed unique mechanical, electrical, and thermal properties, such as very high strength, and high electric and thermal conductance. CNTs have therefore stimulated extensive research, and thermoelectric and sensing characterization of CNTs is yet a novel area of study.

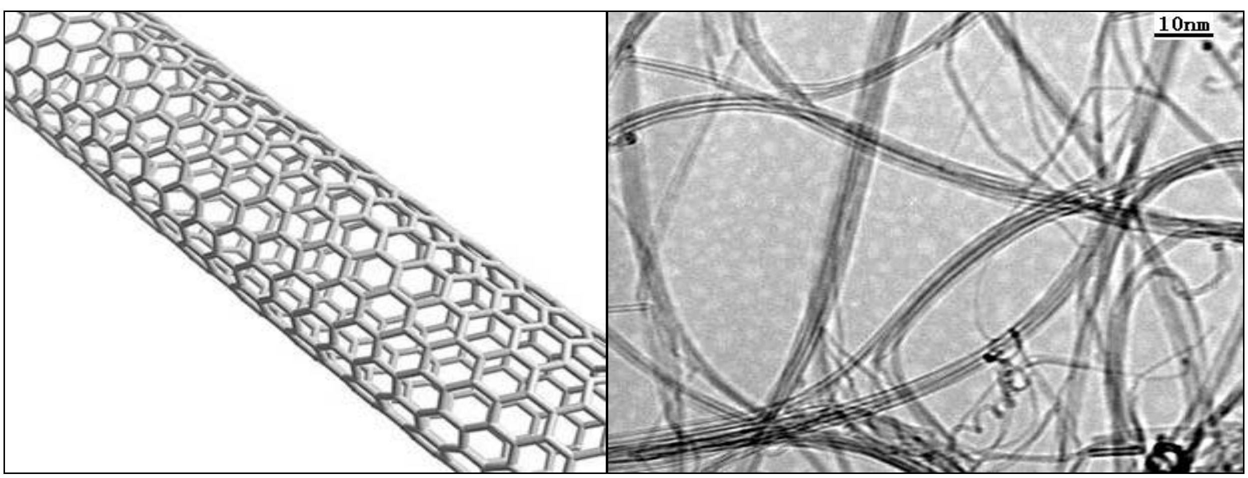

Figure 1.1: Theoretical CNT Nanoscale view and TEM Image of SWNTs.

CNTs encompass major potential on thermoelectric and semiconducting applications. The target therefore, is to develop a multifunctional coating from a variety of carbon nanotubes, and stimulate on the CNT coating the ability to generate emf via a thermoelectric effect. This would potentially allow

monitoring of process conditions and damage sensing capabilities in an industrial-type-application perspective.

1.2 Project Summary

Carbon Nanotube coatings have been investigated and stimulated with multifunctional properties; damage sensing capability through EMF generation, and thermal resistance. CNT properties though, are highly influenced by the direction of the tubes and the synthesis of these, but due to resource constrains, this experimentation was limited to randomly distributed synthesis only. CNTs nonetheless, present a major advantage to the overall objectives of this project, regardless of the random distribution of CNTs (refer to the results and discussion section of this paper for a validation of the preceding statement).

Silicon Carbide nanoparticles are a key in the objectives of this project, as SiC offer excellent corrosion resistance in most chemical environments. Since CNTs have a rather low thermal corrosion (oxidation) resistance (close to 500 °C), depending on the type and tube geometry characteristics, SiC would potentially offer a thermal resistance barrier against thermal corrosion without severely degrading the thermoelectric properties of carbon nanotubes. The investigation extent of this project does not center on the details of corrosion protection towards CNT, but rather focuses on the thermoelectric effects that a SiC layer induces on CNTs films.

The procedure involved dispersing CNTs to a base material such as to create a CNT layer. In contrast to pristine CNTs films, introducing doping impurities would conceptually enhance electrical conduction and thermoelectric behavior. Dopants were introduced on the CNT film through a spin coating and thermal diffusion process. CNT films have been tested within an assortment of CNT variations, (e.g. SWNTs vs MWNTs vs Dopend CNTs, vs SiC layer CNT, etc). Doped and un-doped coating configurations were tested, as well as a variety of dopants, to determine those configurations which improve electric conductivity and a thermoelectric effect. Lastly, thermoelectric measurements were conducted in hot and cool surroundings to simulate a temperature gradient.

1.3 Thesis Organization

Chapter 1 presents an outline of the demand for innovation of sensor like materials for advances in sensor-like materials targeted for energy generation processes. It also presents how carbon nanotubes are a practical option as the material of focus for this project.

Chapter 2 provides the foundation and technical background for the investigation of carbon nanotube thermoelectricity and doping practices.

Chapter 3 describes the progression of the research, and explains how the focus from the general objective to investigate and develop thermoelectric carbon nanotube coatings, is refocused to a more simplistic experimentation, but which can be relevant to broader applications.

Chapter 4 provides an outline of the detailed methodology involved; materials, experimental setup, and experimental measurement methods.

Chapter 5 presents the comparison and justification of thermoelectric characterization results of different carbon nanotube types and configurations.

Chapter 6 summarizes the results and provides the scope for further research.

Chapter 2.0: Literature Review

CNTs can be formed and produced in various types (single-walled, double-walled, and multi-walled), as well as in different chirality and diameter structures. Several research papers have studied carbon nanotubes and their corresponding properties against the various types and the geometrical forms in which these reveal themselves. Studies have shown that CNTs exhibit distinct and unique properties based on their type, alignment, and other geometrical manipulation, but in general, CNTs offer valuable properties attributed to their nanoscale geometry and alignment. Aligning CNTs appropriately and manipulating the geometry characteristics would potentially provide this project a broader scope of possibilities.

Some segments of the subsequent literature review make reference to enhanced properties due to manipulations of geometry, but given the resources of this project, the geometry and alignment was limited (details to be described in later section). Nonetheless, literature research has provided sufficient confidence regardless of the limited parameters, that CNTs yet exhibit appealing characteristics, particularly in a thermoelectric context.

2.1 Properties

2.1.1 Thermal

Carbon nanotubes exhibit higher thermal conductivity along the tube axis in compared to the radial direction (Fig 1). One study stated that the thermal conductivity along the tube's axis is at least two orders of magnitude larger than the radial axis [2]. According to experiments performed, SWNTs revealed a thermal conductivity in the scale of ≈3500 W/·m-K along the tube's axis [3], and ≈1.52 W/·m-K along the radial axis [4]. In a comparative stand point, CNT's along the tube axis, can be largely more conductive than traditional copper (≈ 357 W/m-K), and very thermally insulating along the radial axis, comparable to soil (≈1.5 W/·m-K).

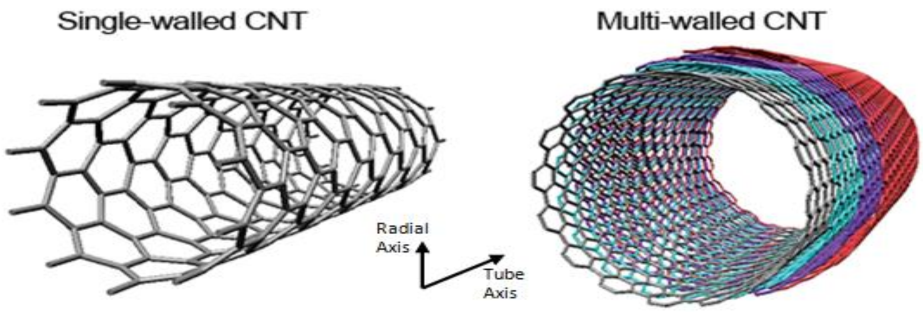

Figure 2.1: SWNT and MWNT with Directional Axes [13].

CNTs materials are also a feasible choice because they have demonstrated to have very high temperature tolerances. It has been found that multi-walled carbon nonotubes (MWNTs) retain theoretical atomic scale stability up to 3200 °K (≈ 2900 °C. An electrical current density was also measured to be1.7x108 A/cm^2 prior to failure [8]. In other experiment, Thostenson. E reported SWNTs to be thermally stable to 2800 °C in vacuum [9]. With this in mind, is it is coherent to assume that CNTs can potentially withstand high temperature conditions.

It has been found that SWNTs are thermally more stable than MWNTs. Multi-walled CNTs are not as thermally stable as SWNTs due to the presence of more than one layer, and when the atoms from different layers start to vibrate at high temperatures, they collide with those of other layers making it easier for MWNTs to disintegrate. With respect to that, our preference towards the type of carbon nanotubes lies with SWNTs. Also, results show that CNTs with larger diameters (d) and shorter lengths (L) are able to withstand higher thermal loads [10].

2.1.2 Mechanical/ Structural

Carbon nonotubes have been found to be the strongest and stiffest material so far discovered in terms of tensile strength (TS) and young modulus (*E*). Experiments have reported SWNT tensile strength and young modulus values of 13-52 Gpa, and 0.32-1.47 TPa respectively. Similarly, reported values for MWNTs were in the range of 11-63 Gpa (TS) and .27-.95 TPa (E) [5]. In comparison, Titatanium-Alloy (Ti-621) has a strength and stiffness of 220 MPa (TS) and 116 GPa (E), making it evident that carbon nanotube's structural properties are significantly higher, and can outperform on many of the mechanical functions commonly rendered by Ti or Ti Alloys.

2.1.3 Electrical

CNTs can be highly conductive based on their structural parameters. Their conductivity has been shown to be a function of their chirality (the degree of twist), their diameter, and lenght. CNTs can be either metallic or semiconducting in their electrical behavior. For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair (n = m) nanotubes are metallic, and nanotubes (6,4), (9,1), etc. are semiconducting [11]. Conductivity in MWNTs is quite complex. Some types of "armchair" structured CNTs appear to conduct better than other metallic CNTs. Furthermore, inter-wall reactions within MWNTs have been found to redistribute the current over individual tubes non-uniformly. However, there is no change in current across different parts of metallic SWNTs. The behavior of the ropes of semi-conducting SWNTs is different, in that the transport current changes abruptly at various positions on the CNTs [14].

An article discussing CNT fibers electrical properties reported electrical resistivity of CNT's under ballistic conditions to be as low as 10^{-6} Ω-cm for SWNTs and 10^{-5} Ω-cm for MWNTs, indicating that CNTs may be better conductors than metals such as copper with a resistance of about1.7 $\times 10^{-6}$ Ω-cm. Also, it has been reported that SWNTs fibers exhibit room temperature resistivities nearly 100 times higher than those of individual SWNTs. Therefore, a suggested approach to improve the electrical conductivity of CNT fibers is to minimize contact resistance between nanotubes by *improving their alignment* and *increasing the lengths* of individual tubes. CNT fibers with an array of .3mm long nanotubes showed conductivity about 22% lower than 1.0 mm nanotubes, indicating that fibers with long nanotube arrays have lower contact resistance. Also, experiments show as in figure 2.2, the temperature dependence of the resistivity and conductivity of a CNT fiber between 75.4 and 300 K. The resistivity decreases monotonically and smoothly from 2.19×10^{-3} Ω-cm at 75.4 K to 1.68×10^{-3} Ω-cm at 300 K. Conversely, the conductivity increases with increasing temperature from 456.6 S-cm^{-1} at 75.4 K, to 595.2 S-cm^{-1} at 300 K, indicating semiconducting behavior [15].

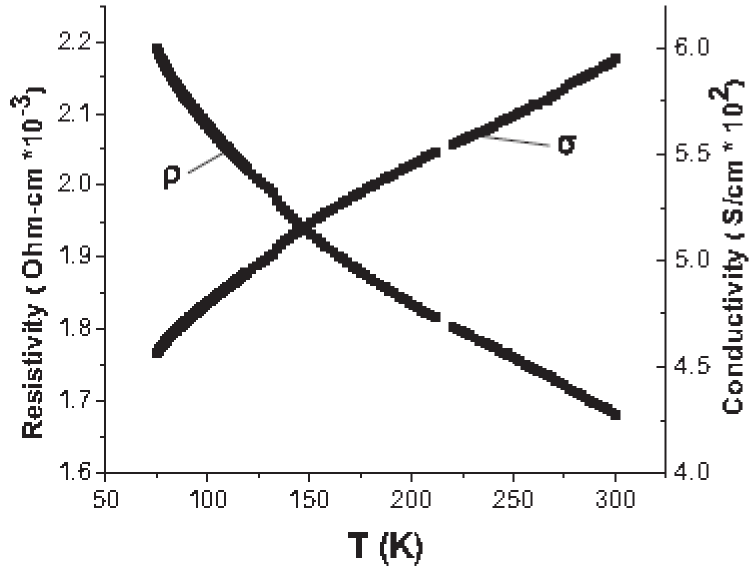

Figure 2.2: Temperature dependence of the resistivity and conductivity of a spun CNT fiber [15].

It is also known that nanotubes contain defects. These defects allow the nanotubes to act as transistors. Likewise, joining CNTs together may form transistor like devices. A nanotube with natural junction (where a metallic section is joined to a semi conducting section) behaves as a rectifying diode [14]. Experiments have shown, however, that pure metallic CNTs lack the thermoelectric effect. Based on the lack of thermoelectric properties on MWNTs, our preferences further incline with semiconducting SWNTs. Additionally, SWNTs have a band gap varying from 0 to 2eV [12], which are comparable values to that of the principal component of today's semiconductor devices "silicon" with a band gap of 1.12eV. Given the prominent semiconducting characteristics of SWNTs, doping CNTs could potentially promote semiconducting behavior.

2.2 Concept

2.2.1 Semiconductor

A semiconductor is a material with electrical conductivity due to electron flow. Electrical current in semiconductors is schematized as being carried either by the flow of negatively charged electrons or by the flow of positively charged holes. In actuality, in both cases only electron movements are involved, but in materials with electron as the minority charge carrier (e.g. a positively charged material), electrons continually leave holes behind making them appear to be moving. The movement of

electrons is rather influenced by a material's electronic band structure, a branch molecular orbital theory and quantum mechanics. In molecular orbital theory, electrons can have energies only within certain bands (i.e. ranges of energy levels) corresponding to a large number of quantum states of the electrons. Electrons in a solid are confined to a number of bands of energy, and forbidden from other regions. Thus, in a semiconductor solid, the energy range where no electron states can exist is referred to as the band gap (Figure 3.3). The band gap generally refers to the energy difference (in eV units) between the valence band and the conduction band. The conduction band, being the range of electron energies higher than that of the valence band, is responsible for conduction of electric current as electrons within this band become mobile charge carriers. The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap, and for this to occur, energy (e.g. thermal energy) is required to lift some electrons to the energy states of the conduction band. Electrons excited to the conduction band also leave behind electron holes in the valence band, and so the conduction band electrons and the valence band holes contribute to the overall electrical conductivity of a semiconductor material.

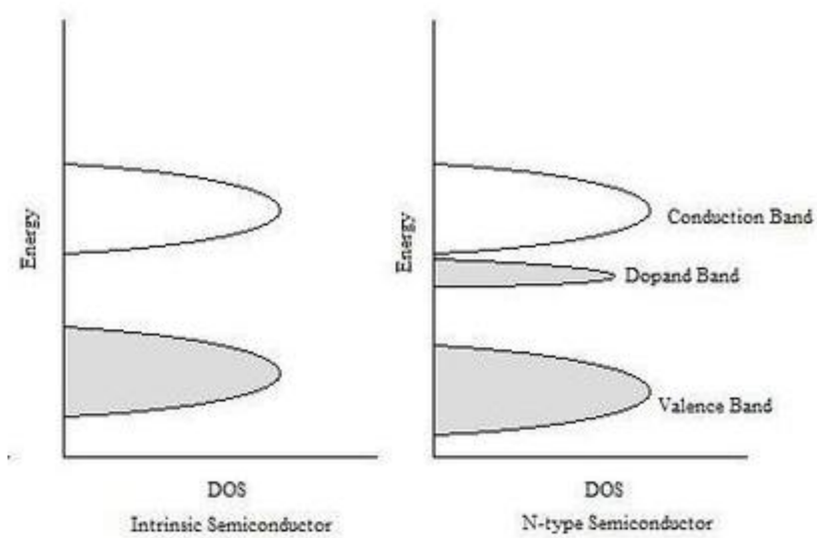

Figure 2.3: Representative density of states of semiconductor and n-doped semiconductors. [17].

2.2.2 DOPING

The process of adding controlled impurities to a semiconductor is known as doping; with dopants classified either as electron acceptors (holes as majority carriers) or donors (electrons as majority carriers). Semiconductors doped with donor impurities are called n-type, while those doped with acceptor impurities are called p-type. Doping a semiconductor introduces allowed energy states within the band gap (Figure 2.3), and very close to the energy band that corresponds to the dopant type. Donor impurities create states near the conduction band while acceptors create states near the valence band. Electrons at these states can be excited to the conduction band, becoming free mobile electrons and consequently promoting electrical current. A substance's Fermi level can be thought of as the energy up to which available electron states are occupied. Dopants, therefore, have the effect of shifting the material's Fermi level towards the energy band that corresponds to the dopant with the greatest concentration.

A p–n junction is formed by joining p-type and n-type semiconductors together in very close contact. As a result, and in a simplified standpoint, electrons and holes near the p–n interface may cross to the opposite region and begin a recombination process that generates electrical current. A p-n junction, by its own, instantly attains electric stability due to the immediate creation of a depletion region, which impedes the crossing and recombination of electrons to the opposite side. An applied forward bias voltage, however, lifts the electrons energy states and forces electrons and holes against the depletion region. The depletion region is therefore reduced enough, permitting charge carriers to cross and recombine, and electricity is generated in as in a closed circuit. Similarly, as temperature rises, there is more energy to lift electrons into the energy states of the conduction band, and so, a similar process as with the applied voltage occurs. The dependence of the electron energy distribution on temperature explains why the conductivity of a semiconductor has a strong temperature dependency.

Doping of CNTs has been extensively explored, and thus it is safe to deduce that p-type and n-type doped CNTs demonstrate semiconductor-like characteristics and exhibit thermoelectric properties, particularly with a p-n junction arrangement. Experiments from other publications in this subject showed that encapsulating two kinds of atoms or molecules, namely both electron donors and acceptors in one Double Walled Carbon Nanotube (DWNTs) provides a possibility of creating ideal p-n junctions.

DWNTs were found to exhibit diode behavior, greatly increased by encapsulating C_{60} (p-type) and Cs (n-type) [6]. In an investigation performed by S.M. Mirza and H. Grebel, they examined the thermoelectric properties of SWNT films composed of co-aligned, cross-aligned and randomly dispersed p-n junctions. P-n junction samples were also tested, and results showed that the developed voltage for side-by-side, cross aligned p-n junctions was almost 7 times larger (3.3mV) than the prior p-type randomly or along axis oriented samples (.5mV). Thus, the side-by-side, cross aligned p-n junction configuration suggests having an advantage of the overall thermoelectric effect [7], despite the fact that this configuration did not offer the lowest electric resistivity. The developed current must have compensated the higher resistivity according to ohm's law (V=IR).

2.2.3 Thermoelectric Effect

The thermoelectric effect (a.k.a thermoelectric power) is the direct conversion of temperature difference to an electric voltage. According to electronic band theory of solids, thermoelectric power is a measure of the electrical potential developed when a temperature gradient is applied across the sample due to migration of the higher-energy-level electrons (hot side) to a lower-energy level (cooler side) of the sample. As a result, a potential difference is set up across the sample which can be measured. Thermoelectric power is directly related to the potential energy at the Fermi energy. Similarly, dopant atoms may emit or absorb electrons depending on the relation between the highest occupied molecular orbital/lowest occupied molecular (HOMO/LUMO) level of the dopant atom and the Fermi Level of the CNT. When CNTs are exposed to these materials, the Fermi level rises in case of donors and lowers in case acceptors [18]. In a simple point of view, an applied temperature gradient causes charged carriers (electrons or holes) in the material to diffuse from the hot side to the cold side and a process occurs as suggested in the doping section.

A thermocouple is a device consisting of two different conductors (usually metal alloys) that produce a voltage proportional to a temperature difference between either ends of the pair of conductors. Any junction of dissimilar metals will produce an electric potential related to temperature. As explained previously, any conductor subjected to a thermal gradient will generate a voltage know as the thermoelectric effect. Any attempt to measure this voltage necessarily involves connecting another

conductor to the "hot" end. This additional conductor will then also experience the temperature gradient, and develop a voltage of its own which will oppose the original, and the magnitude of the effect depends on the metal in use. Using a dissimilar metal to complete the circuit creates a circuit in which the two legs generate different voltages, leaving a small difference in voltage available for measurement. That difference increases with temperature. A thermocouple can produce current, which means it can be used to drive some processes directly, without the need for extra circuitry and power sources [19].

Chapter 3.0: Research Growth and Refocus

The original target of the project was to investigate CNTs as a protective coating material, and explore and stimulate multifunctional properties such as damage sensing through of EMF generation, and thermal and structural protection to a base material. The objective involved the adhesion of carbon nanotubes into typical turbine material (tungsten or titanium alloys), and implement a doping process, similar to silicon doping methods, which are widely used in the semiconductor industry. Given that CNTs offer unique thermal, structural, and electrical properties based on their geometry and alignment synthesis, the above target was envisioned and seemingly possible through the manipulation and variation of those parameters. However, the complexity to bond CNTs to a base material and controlling alignment and geometry at this early stage of the research, forced narrowing the research to a thermoelectricity focus as a start point.

Throughout the course of the project, and as the plan refocused to thermoelectricity study, the experimentation led to a set up and measurement method analogous to thermocouple theory. This set up resulted as the only feasible method for measuring thermoelectricity, given the nature of this experimentation. It was established that carbon nanotubes act as conductor, similarly to other metals or alloys. Carbon nanotubes are manufactured in powder form, and involve dispersion in an inorganic solution. These solutions permit CNTs to be dispersed essentially in any surface, and can potentially be part of an alloy or ceramic composite. Note that the scope of this project does not entail any CNTs alloy or ceramic composite exploration. The experimentation targeted specifically on CNTs, to develop a solid understanding of pristine carbon nanotube thermoelectric properties, and structure a basis for future work, possibly with CNT alloys, and/or composites.

Doping, being part of the objectives of this research involve CNTs to be exposed to relatively high temperatures due to a thermal doping diffusion processes (e.g. ≈ 900 °C). Similarly, another aim was to test thermoelectric properties inside a wider temperature range (e.g 25 °C to 900 °C ± 100). These high temperature conditions implicate possible oxidation of carbon nanotubes. For that reason, silicon carbide (SiC) nanoparticles were introduced in the study; to exploit its effects on

thermoelectricity, if it were utilized as a protective layer to CNTs, provided that silicon carbide is thermally resistive to corrosion (oxidation).

Chapter 4.0: Experimental Procedure and Design

4.1 Materials and Equipment

Carbon Nanotubes – The materials most involved in the concept of this research are CNTs (SWNTs and MWNTs). SWNTs were produced and manufactured by cheaptubes Inc. These are 99% pure SWNTs consisting of approximately 60% semiconducting 40% metallic tubes, with <2% MWNTs and graphite content according to cheaptubes Inc MSDS. Outer Diameter of the tubes is 1-2 nm, and inner diameter of .08-1.6 nm, and lengths 3-30 μm. MWNTs were obtained from previous research, with 95% MWNT purity and outer diameter of about 20-30 nm.

Silicon Carbide Nanoparticles – SiC nanoparticles were also obtained from previous research. The approximate size of the nanoparticles is about 30 nm based on a data assessment of SiC manufactures, but the precise purity is unknown.

Alumel Wire – Alumel (Ni-Al) wire was used to create the dissimilar metal junctions to form a thermocouple-like design for the measurement of thermoelectricity. Note that thermoelectric results in this thermocouple-like design depend also on the dissimilar metal. Alumel was chosen because it is one of the wires found in a k-type thermocouple, and it was readily available in the lab, but mainly because it is resistant up to about 1200 °C, whereas typical copper wire would corrode.

Silver Solder – Silver epoxy is a cold solder conductive adhesive used to solder the CNTs film surface to the alumel wires. Silver epoxy was manufactured by MG Chemical (Figure 4.1).

Figure 4.1: Silver Epoxy for Conductive Soldering

Alumina – Alumina is a thermal insulative ceramic and non-electrically conductive material. Alumina was used as insulation of a high temperature ceramic heater plate utilized to conduct higher temperature measurements (700 – 900 °C) not attainable with a typical lab heater plate. Alumina was also used as a substrate alternative to glass and quartz for performing CNT doping and thermoelectric measurements of these. The reasoning is that alumina has a porous surface that enable CNT solution to penetrate deeper and adhere better to the surface, whereas with glass/quartz, doping solutions and a hot environment would typically break the film.

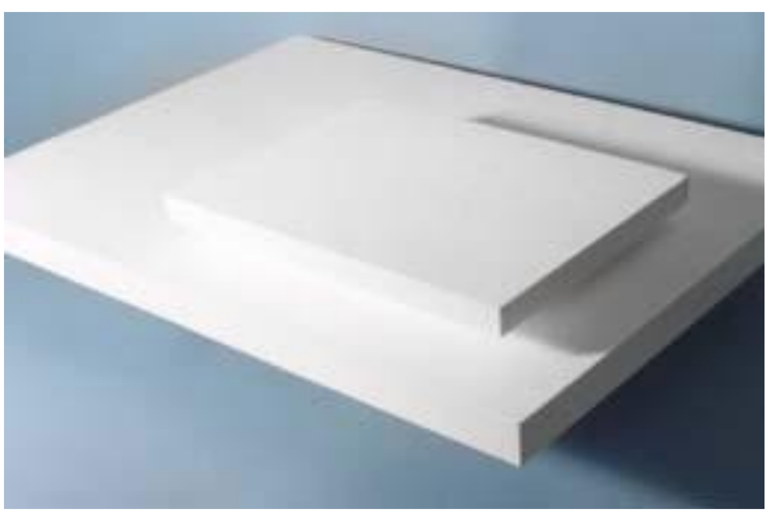

Figure 4.2: Alumina Insulation Board

Ultrasonic Sonicator – A Sonicator-Ultrasonic Processor (Branson Sonifier 450) was utilized to disperse carbon nantubes in a solvent solution (ethanol).

Data Acquisition System – The data acquisition system include: An NI USB-9211 Analog Output Module (USB DAC) was used along side K-thermocouples to record temperature measurements at 1 hz. An NI X series Data-logging pci (PCI DAC) together with an NI SCB-68 connector block device was used to record voltage measurements. Temperature and voltage measurements are integrated in parallel through Lab View Signal Express software.

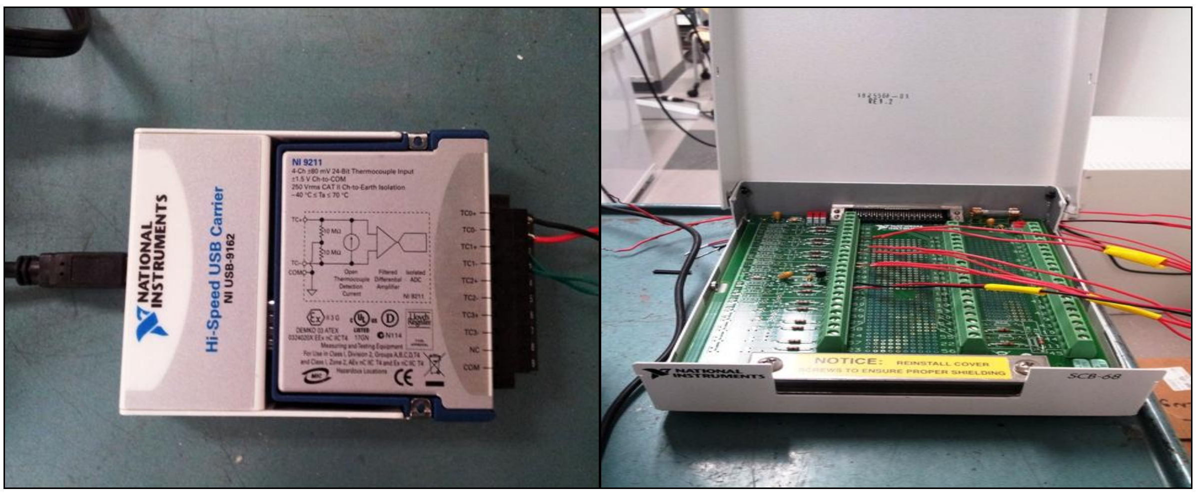

Figure 4.3: Data Acquisition System. Thermocouple DAC (left), and Voltage DAC (right)

Hot Surface Device – A lab-type hot plate (hp-a1915B) and ceramic heater plate (CRHP-12650/230-E-A) were utilized for hot surface temperature control. An ultra high temperature heating tape was utilized to induce high surface temperature to doped CNT films, since these measurements involved heat concentrated on the middle of the CNT layer as opposed to one of the ends.

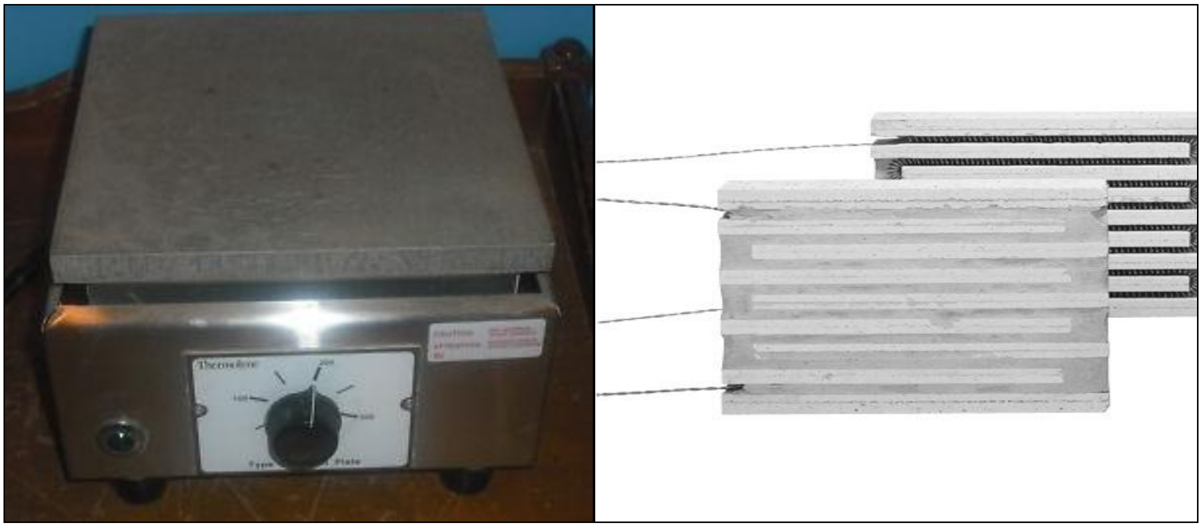

Figure 4.4: Lab-type low temperature hot plate (right). High temperature ceramic heater (right).

4.2 Sample Preparation

Preparation of all the samples involved an identical or a similar procedure.

CNTs as well as SiC nanoparticles were supplied in dry powder form (figure 4.5), but powders offer minimum functionality. Thus, CNT and SiC solutions were prepared by disperstion of the nanoparticles in an ethanol solution. Ethanol does not affect the molecular structure of the nanoparticles and enable uniform dispersion throughout the solution. Dispersion is carried out through sonication with an ultrasonic probe, to break intermolecular interactions and molecular entanglements (figure 4.6). An analogous example would be stirring cocoa powder and milk, with the difference that nanoparticles do not dissolve in ethanol, but rather disperse. The exercised ratio concentration of nanoparticle powder to ethanol solution was 50 mg of powder to 50 ml of Ethanol. This ratio concentration allowed a uniform dispersion of the nanoparticles. Sonication was performed for approximately 15 min at an amplitude setting of 70 to 80 %, with 10 sec pauses after 30 sec runs.

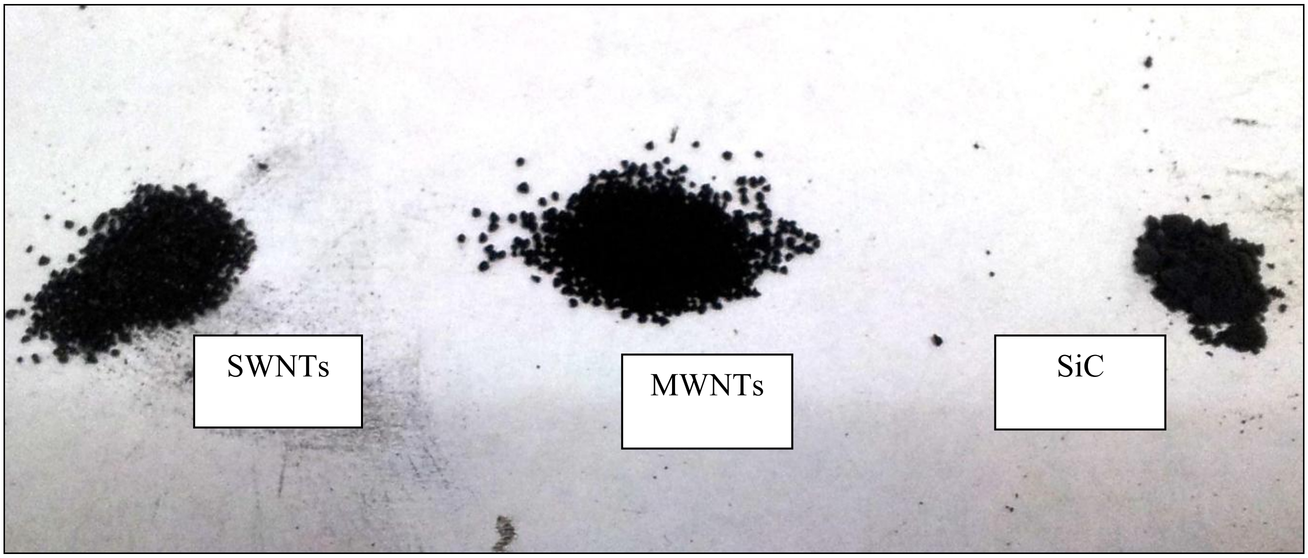

Figure 4.5: Supplied form of SWNTs, MWNTs and SiC in dry power appearance (from left to right respectively)

Figure 4.6 shows the sonication set up, and Figure 4.7 illustrates a depiction of CNT dispersion in ethanol before a after sonication process.

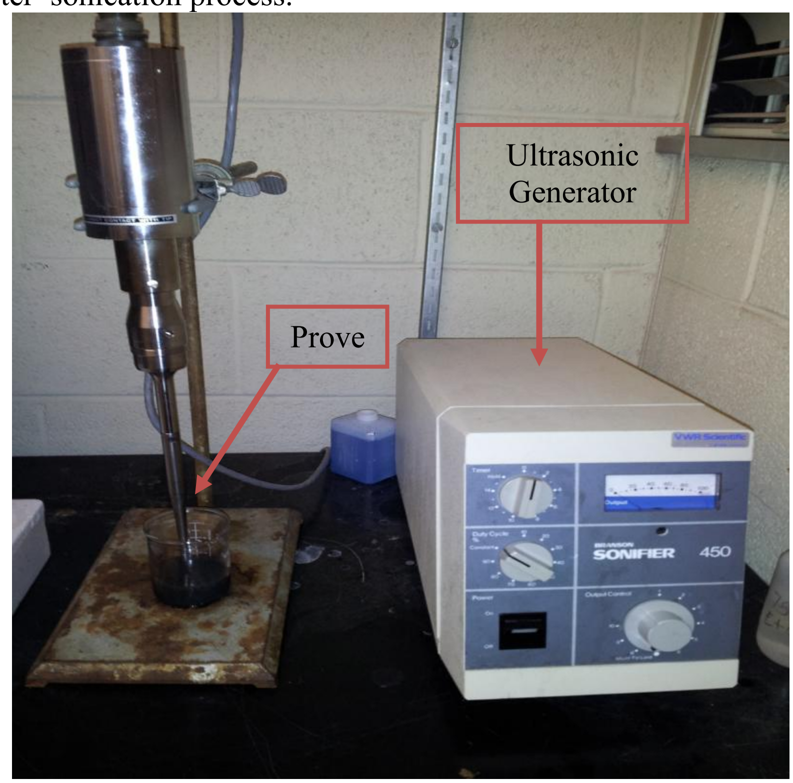

Figure 4.6: Sonicator-Ultrasonic Processor

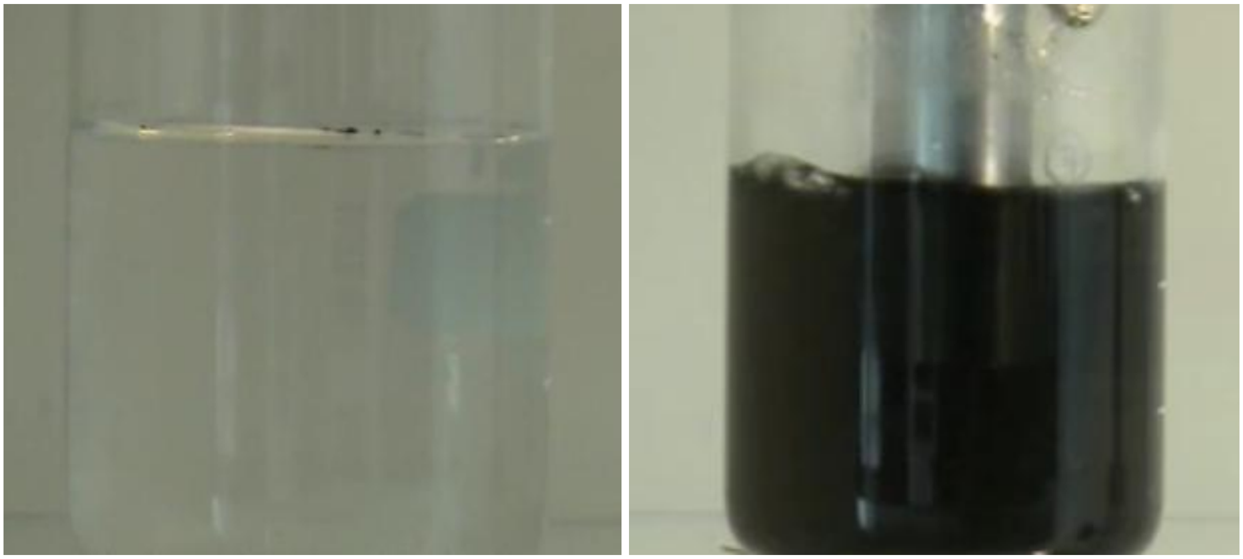

Figure 4.7: Before and After Depiction of Dispersed Carbon Nanotubes

Preparation of a CNT or SiC layered substrate involves deposition of the CNT or SiC solution onto the substrate or target surface. This was done using a nozzle to pour solution coating (Figure 4.8). Though, filtering out some of the ethanol with paper, before pouring the nanoparticle solutions, leaves behind a more viscous nanoparticle solution to facilitate a more consistent layer. Lastly, the layered substrate is placed on the hot plate and left for baking to rid the remaining ethanol.

Figure 4.8: Deposited CNT layer

The nanoparticle substrate circuit is finalized by emplacing alumina wires at opposite ends along the length of the layer as depicted in Figure 4.9, and soldered in place with conductive silver epoxy. Silver expoxy took an average of 1-2 hrs to dry in room temperature.

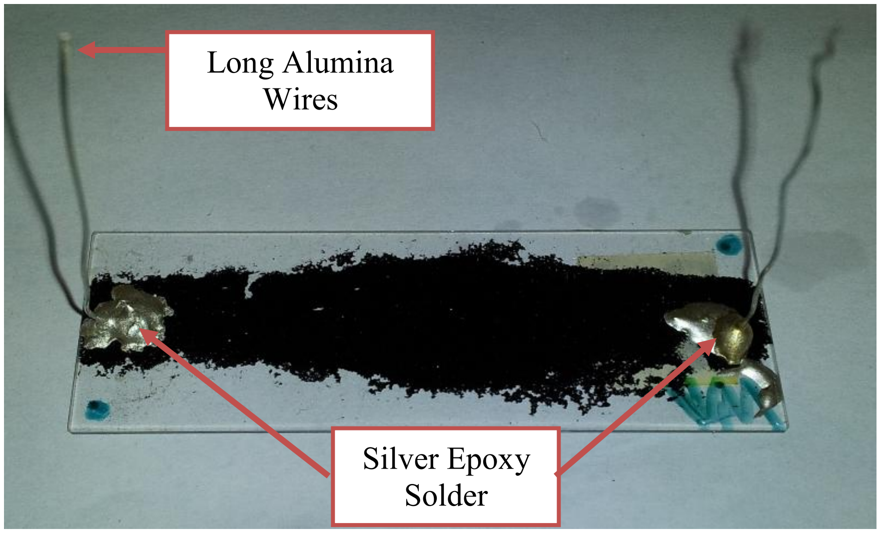

Figure 4.9: Finalized Sample for Thermoelectric Measurements

4.3 Experimental Design and Measurement Methods

4.3.1 Low Temperature Thermoelectric Measurements

Low temperature thermoelectric measurements were conducted within a temperature range of 25 to 200 °C. The ceramic heater plate could have replaced the lab-type hot plate for most thermoelectric measurements, but lower temperature experiments were carried out with the only readily available hot plate (lab-type heater plate) at that time.

The set up consists of emplacing the glass/quartz substrate on top of the hot plate and a cool surface (ice pack, dry ice, etc), with one of soldered junctions on top of the hot side and the other on the cool side. This setup would replicate a cold and hot junction configuration analogous to a thermocouple measurement (refer to figure 4.10 and 4.11). The alumina wires must be long enough and suggestively the same size, such that the connecting wires feeding the data acquisition system or multimeter are away of the of the high temperature medium. This will ensure that the junctions between the alumina and the connecting wires, and the circuit inside the multimeter are at the same temperature, otherwise different temperatures would introduce measurement error. Two thermocouples are also emplaced at both hot

and cold junctions as depicted on figure 4.11. These thermocouples feed to the data acquisition system as well as the alligator clamps wires connecting to the alumina wires. LabView Express is used to record both voltage and temperature data, and integrates both measurements for later export to an excel file.

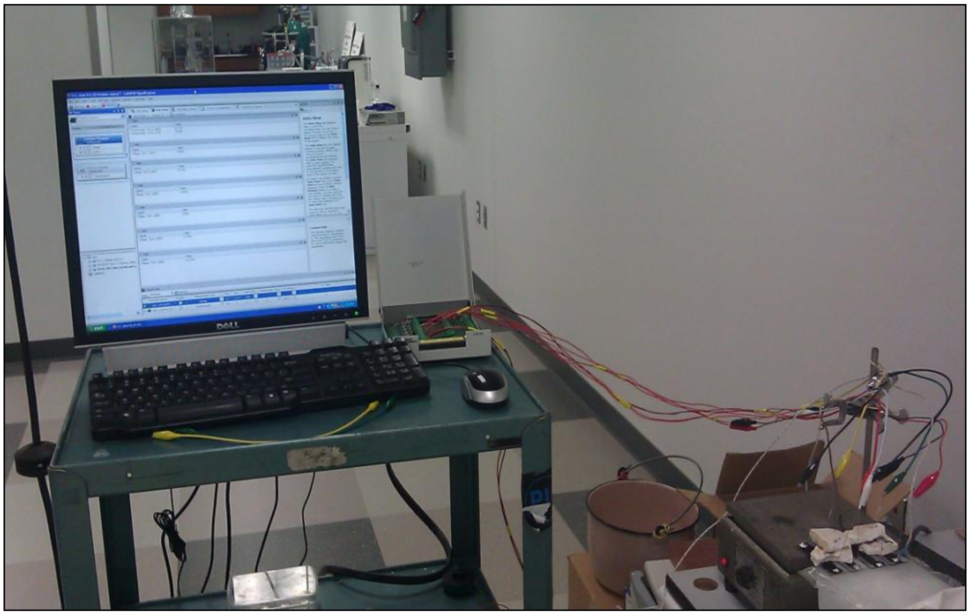

Figure 4.10: Wide view of experimental setup

Figure 4.11: Hot/cold substrate setup with, depiction of connecting wires and thermocouples

The measurement method exemplified above was used for voltage vs temperature measurements only because the data acquisition system requires a special integrated circuit to measure current and resistance. To measure current and resistance vs temperature, the experimental setup is the same with the exception of the data acquisition system. In this case, wires and thermocouples that feed to the data acquisition system, would feed to multiple multimeters (number depend on the number of samples), and values are observed and recorded by the experimenter himself. Voltage vs temperature can also be recorded this fashion, but the DAC facilitates the measurements.

4.3.2 High Temperature Thermoelectric Measurements

High temperature thermoelectric measurements follow an identical experimental setup as that from the low temperature counterpart. The only difference is the heating unit and its operation. High temperature measurements are carried out by a ceramic heater plate capable of reaching of a maximum surface temperature ≈980 °C if well insulated. The heating plate surface was thoroughly insulted with alumina boards, except at the hot ends of the substrate (figure 4.12). Alumina insulation limited the amount of heat lost the environment through heat transfer, and allowed the surface to reach a temperature of about 700-800 °C. The ceramic heater plate temperature was controlled with a CN7833 Omega Inc controller, and the power supply 240 V – 30 A (needed for operation of the heater) was regulated with a solid state (SSRL240AC25) relay, also supplied by omega inc.

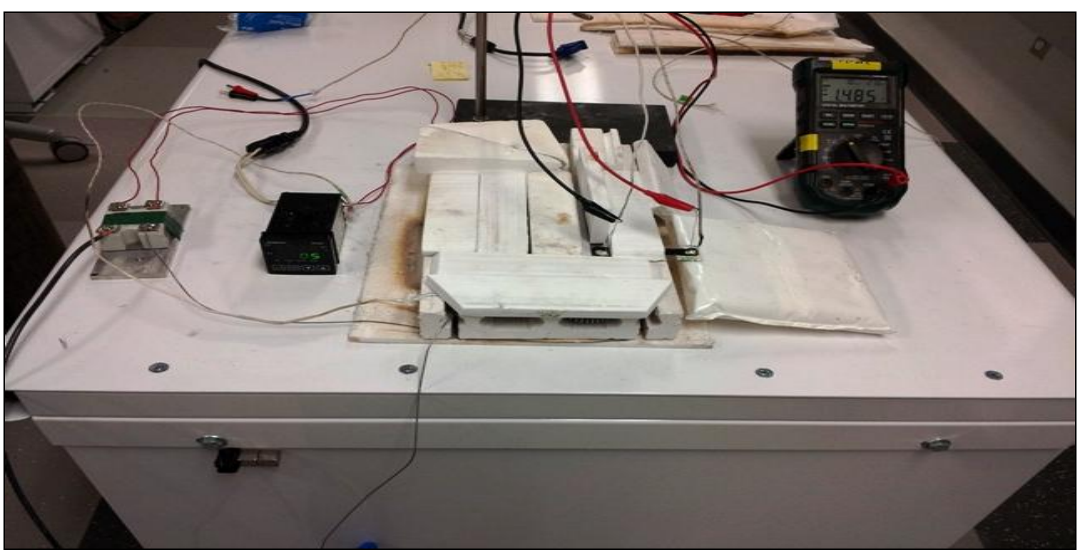

Figure 4.12: High Temperature Thermoelectric Measurement Setup

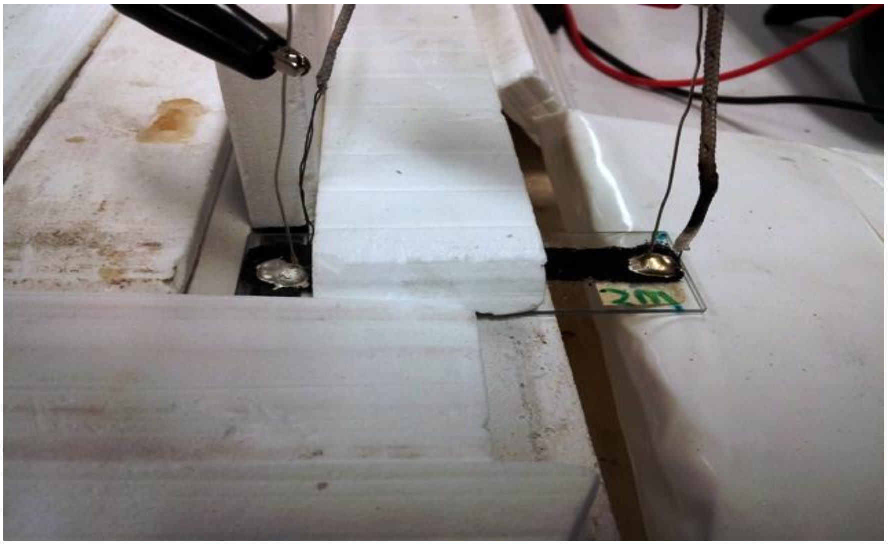

Figure 4.13: Figure 4.12 close up

Chapter 5.0: Results and Discussion

5.1 Low Temperature Tests

The thermoelectric responses of SWNTs are depicted in Figures 5.1, 5.2, & 5.3, and MWNTs are depicted in Figures 5.4, 5.5, & 5.6 for voltage, current, and resistance variables respectively. These graphs compare replicate CNT naoparticle samples to attain assurance that replicates provide equivalent results, and are not affected by the random distribution of the CNTs, or by deposition discrepancy.

5.1.1 Low Temperature Assurance Test for SWNTs

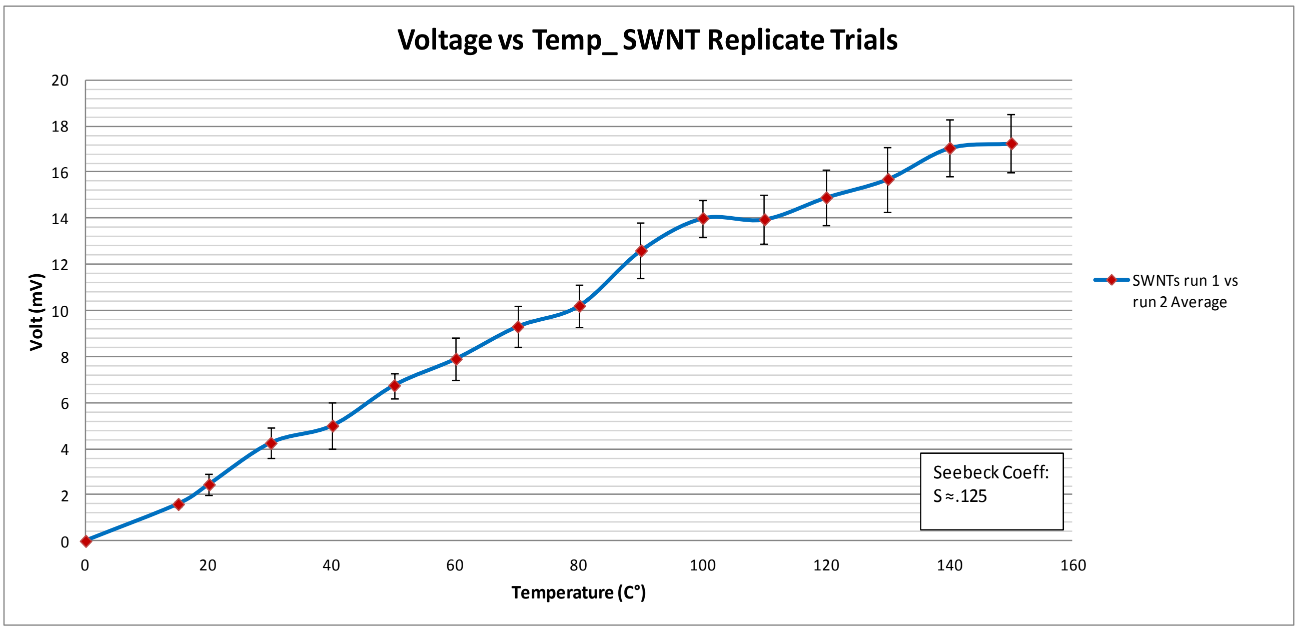

Figure 5.1: SWNTs voltage vs temp replica test.

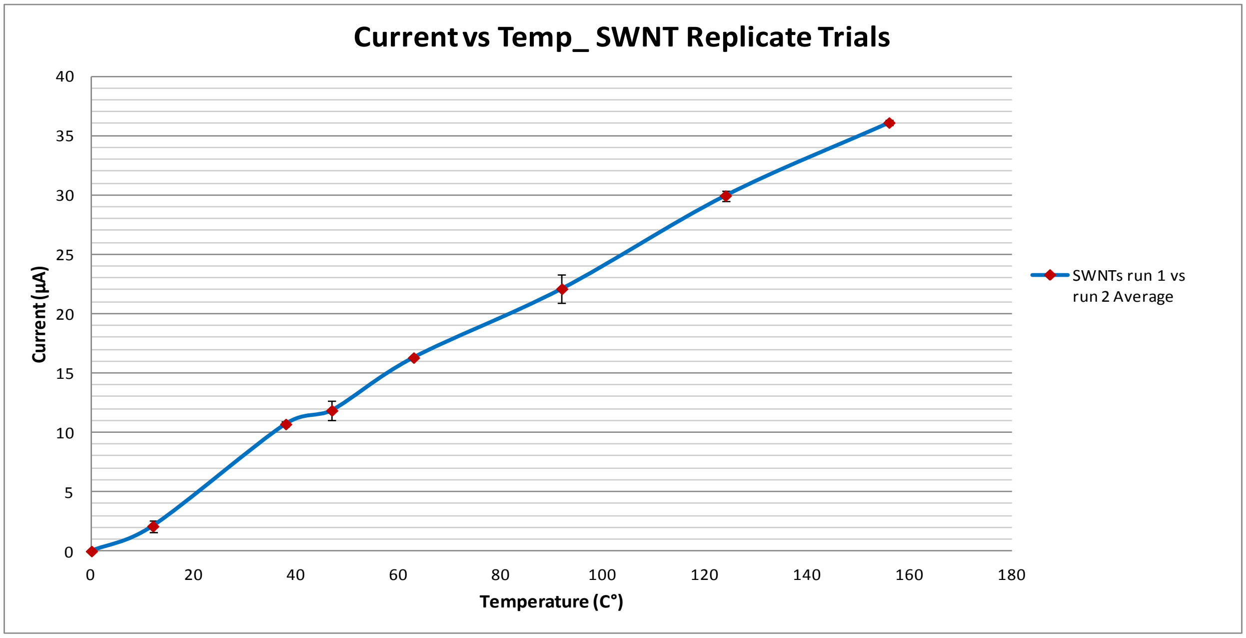

Figure 5.2: SWNTs current vs temp replica test.

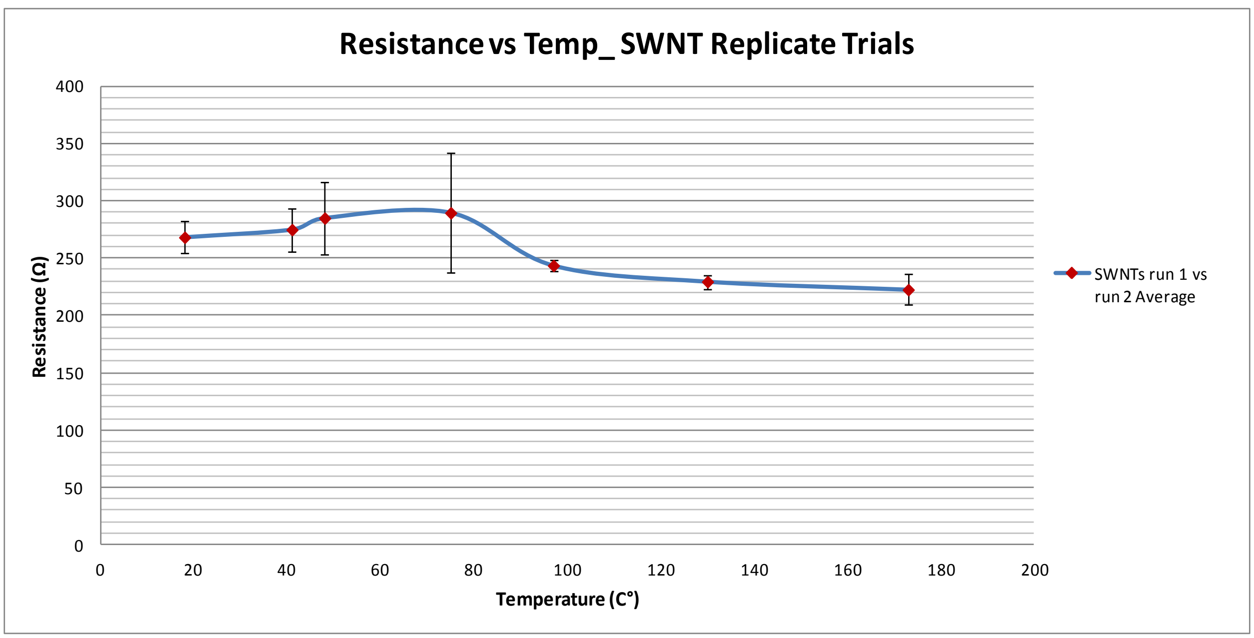

Figure 5.3: SWNTs current vs temp replica test

5.1.2 Low Temperature Assurance Test for MWNTs

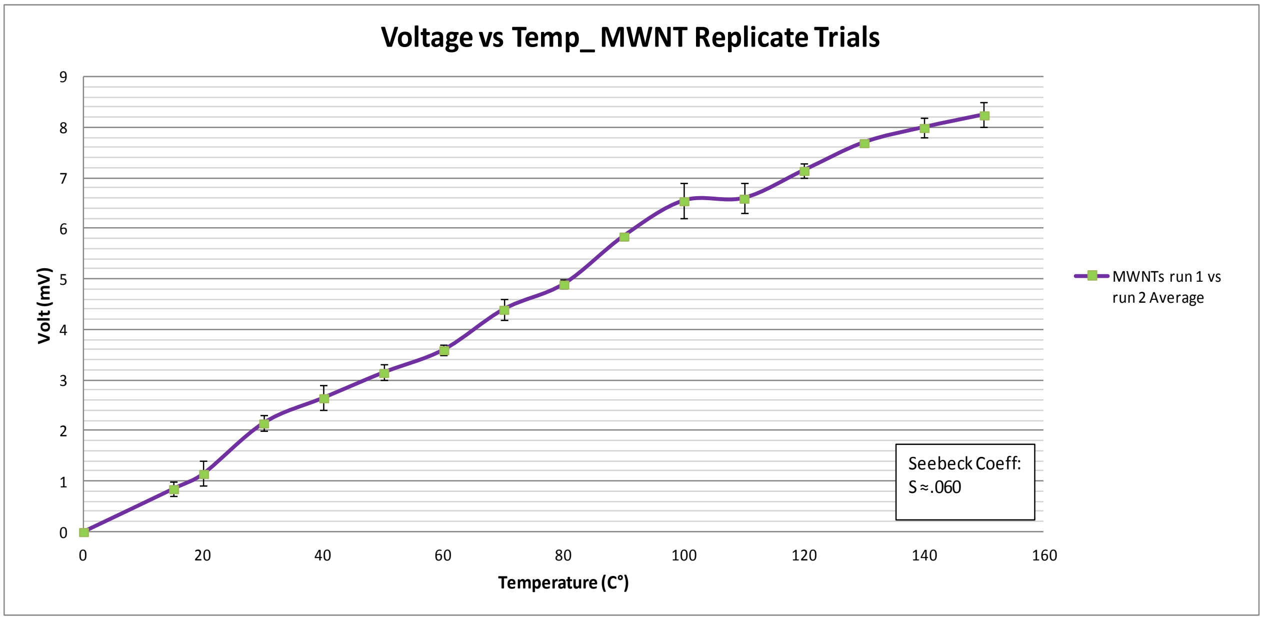

Figure 5.4: MWNTs Voltage vs temp replica test

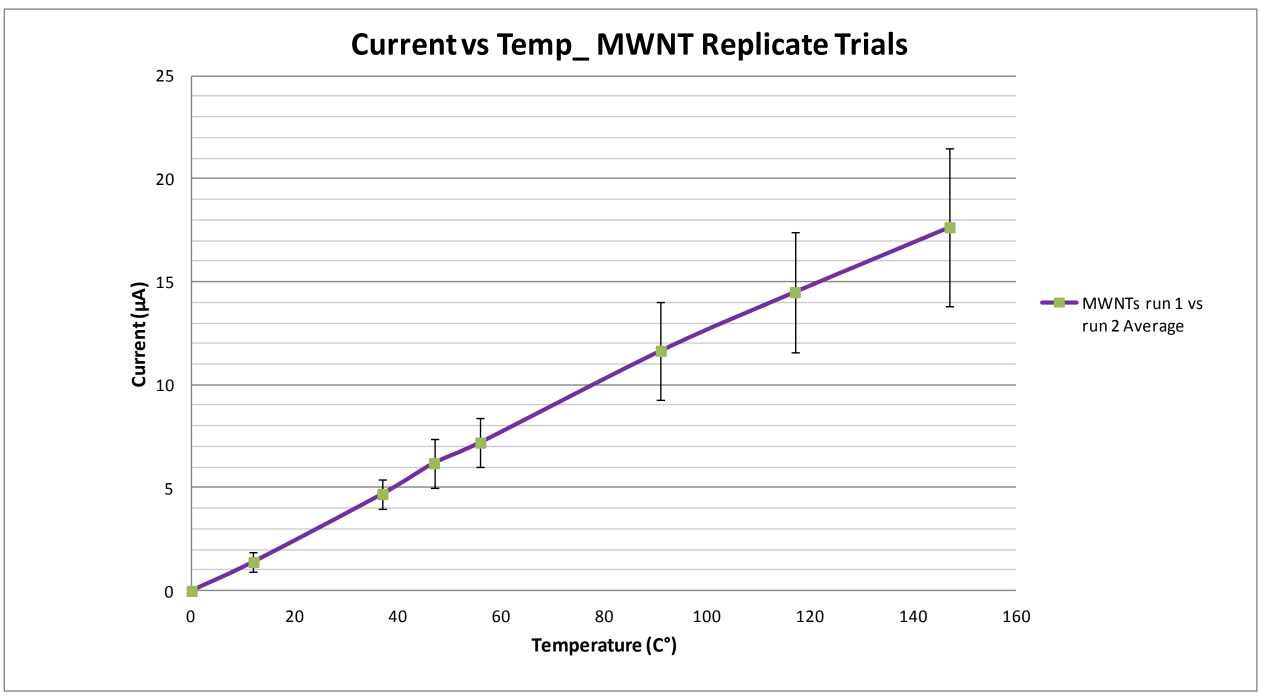

Figure 5.5: MWNTs Current vs temp replica test

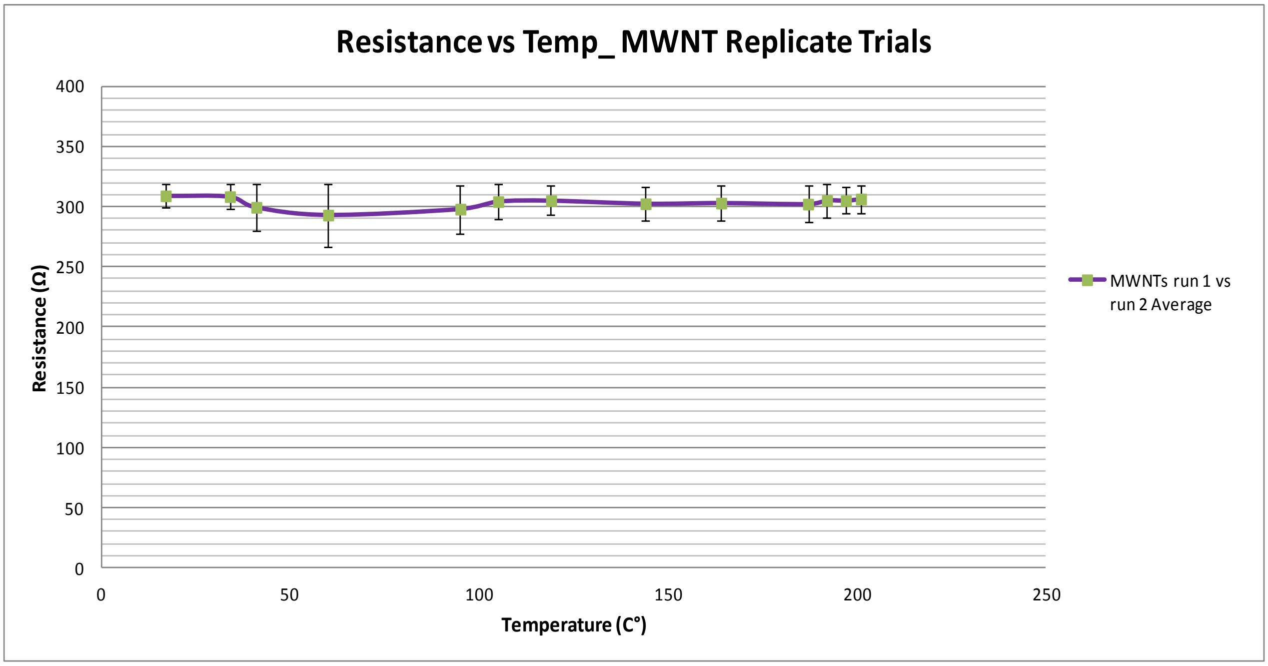

Figure 5.6: MWNTs Resistance vs temp replica test

The diverged results observed with MWTNs are due to human error and differences in the setup. For instance, up to 4 or 5 samples were tested in conjunction, and the surface temperature of the hot and cool sides might have been slightly different. The measured temperatures were also averaged among the tested samples, and this is also might have introduced minor discrepancies.

5.1.3 Thermoelectric Measurement Comparison between SWNTs vs MWNTs

Figures 5.7, 5.8, & 5.9 contrast the thermoelectric properties of SWNTs vs MWNTs.

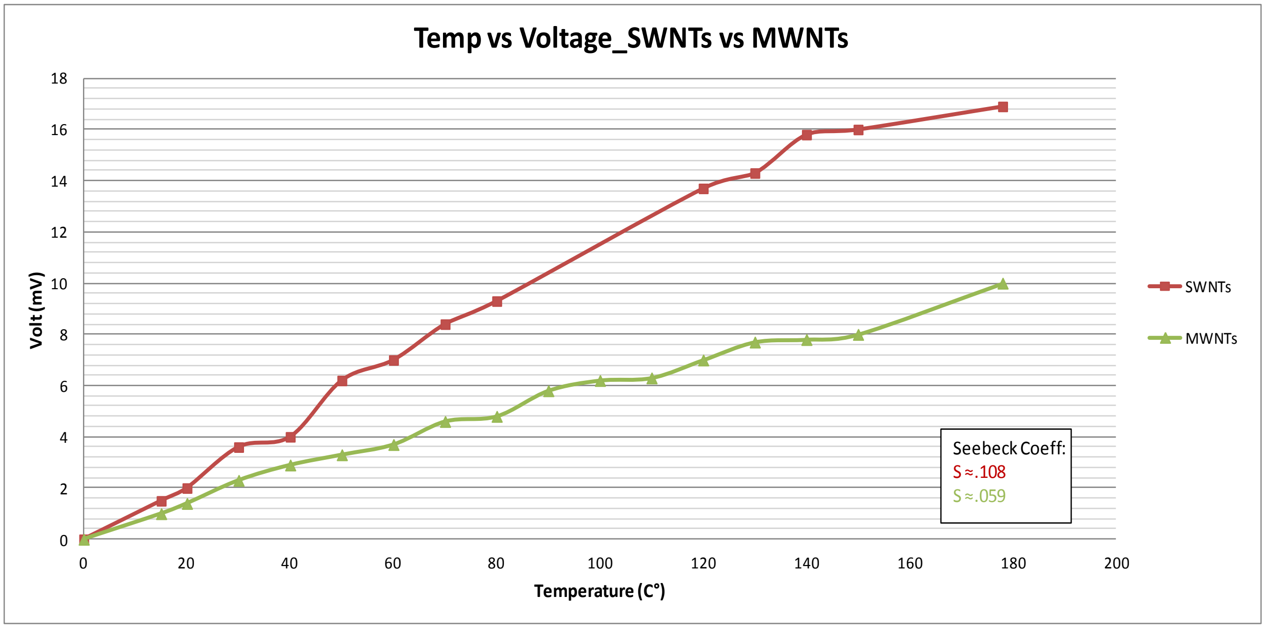

Figure 5.7: Voltage vs Temp, SWNTs vs MWNTs

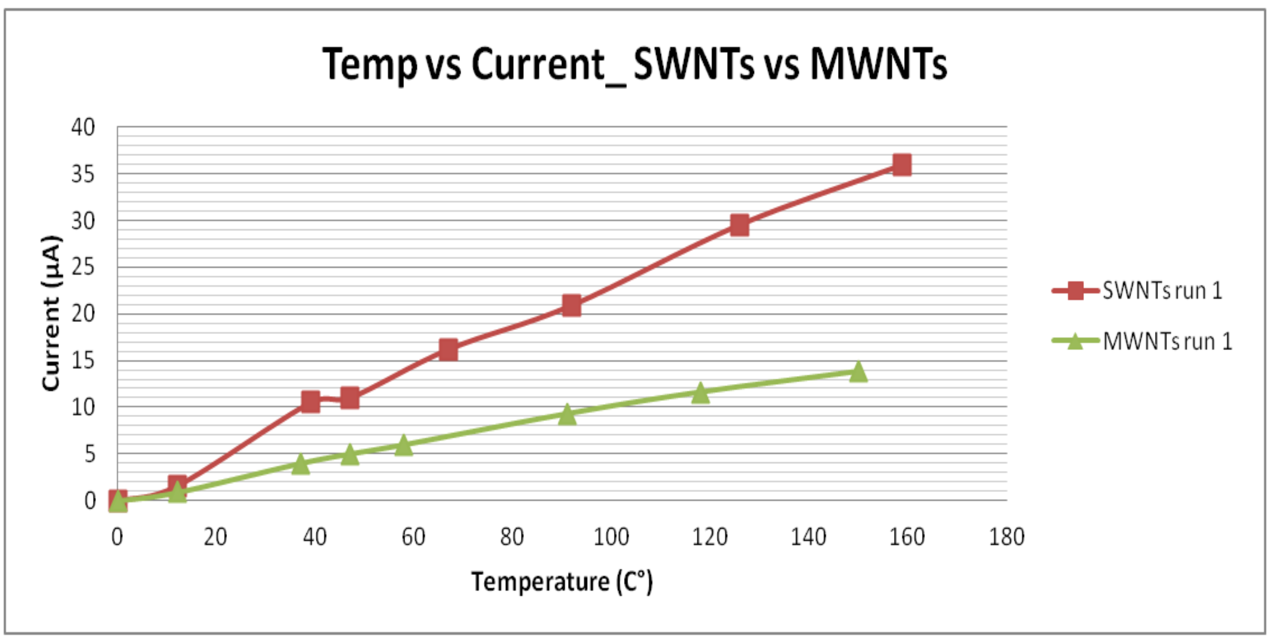

Figure 5.8: Current vs Temp, SWNTs vs MWNTs

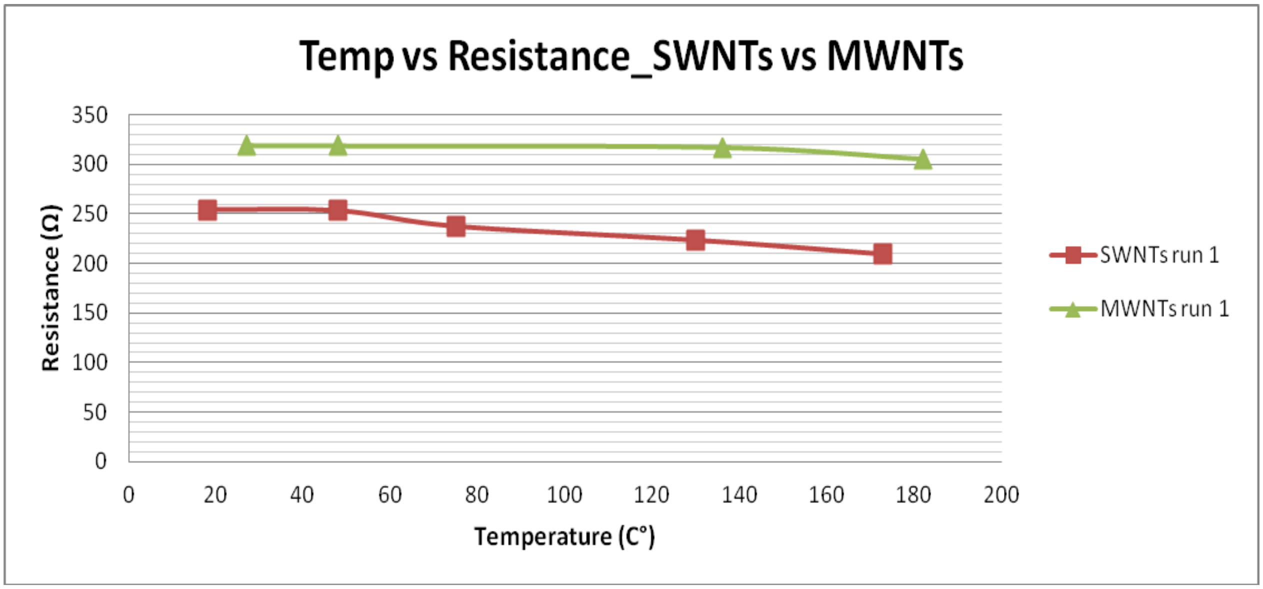

Figure 5.9: Current vs Temp, SWNTs vs MWNTs.

Figures 5.7, 5.8, & 5.9 reveal SWNTs outperform MWNTs for all electrical variables (V, A, & R), with a Seebeck coefficient approximately double that of MWNTs. This indicates that the rate of change for voltage and current is approximatelly twice the magnitude from that of MWNTs. Similarly, power production (noting that P= V × I, and resistance remains constant) is be approximately twice the magnitude for SWNTs in contrast to MWNTs.

5.1.4 Thermoelectric Measurements Comparison Between SWNTs and SWNTs w/ SiC Layer

Figures 5.10, 5.11, & 5.12 contrast the thermoelectric properties of SWNTs vs SWNTs with a SiC layer.

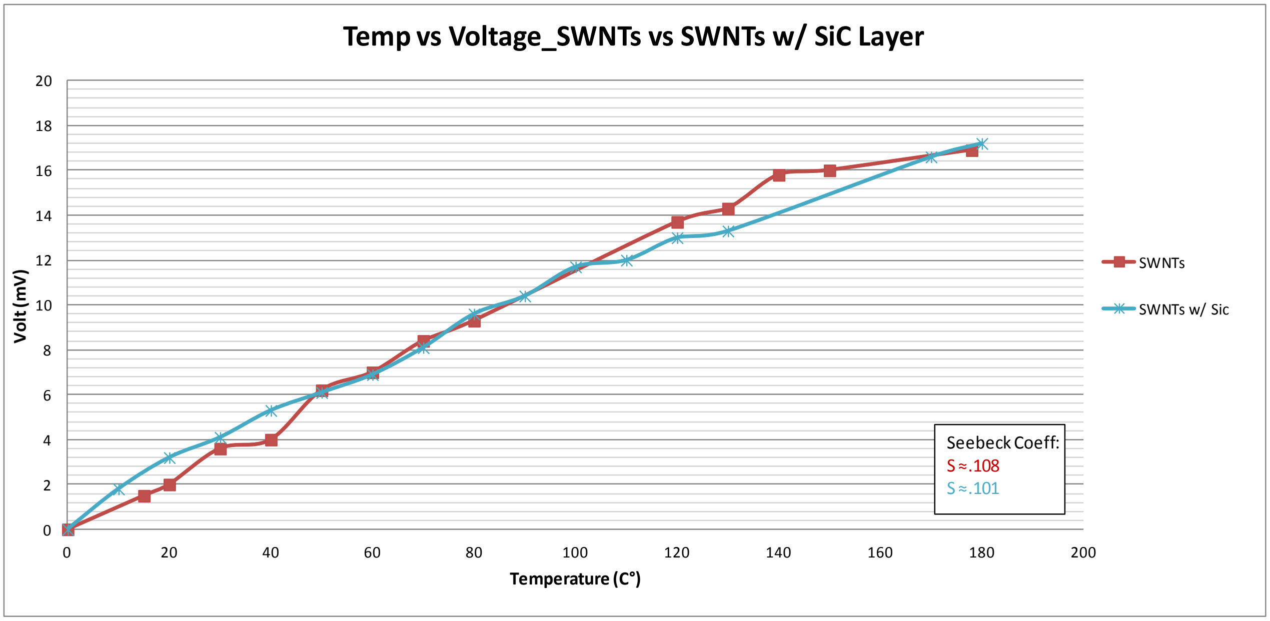

Figure 5.10: Voltage vs Temp, SWNTs vs SWNTs w/ a SiC top Layer

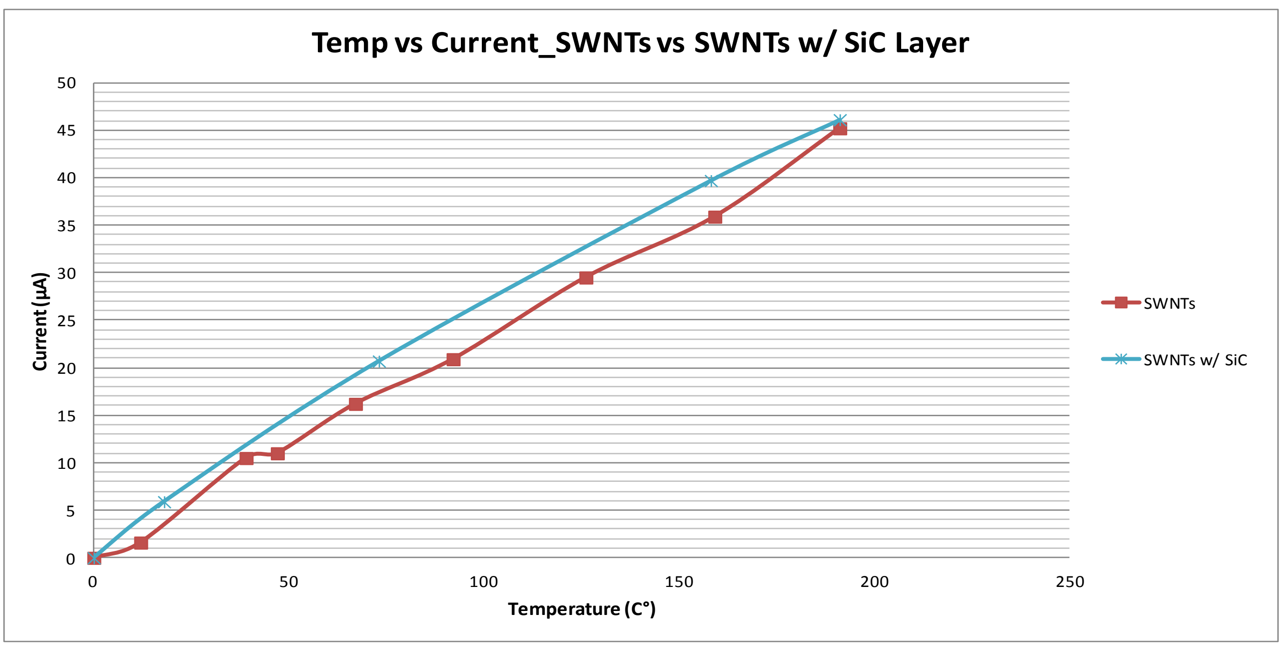

Figure 5.11: Current vs Temp, SWNTs vs SWNTs w/ a SiC top Layer

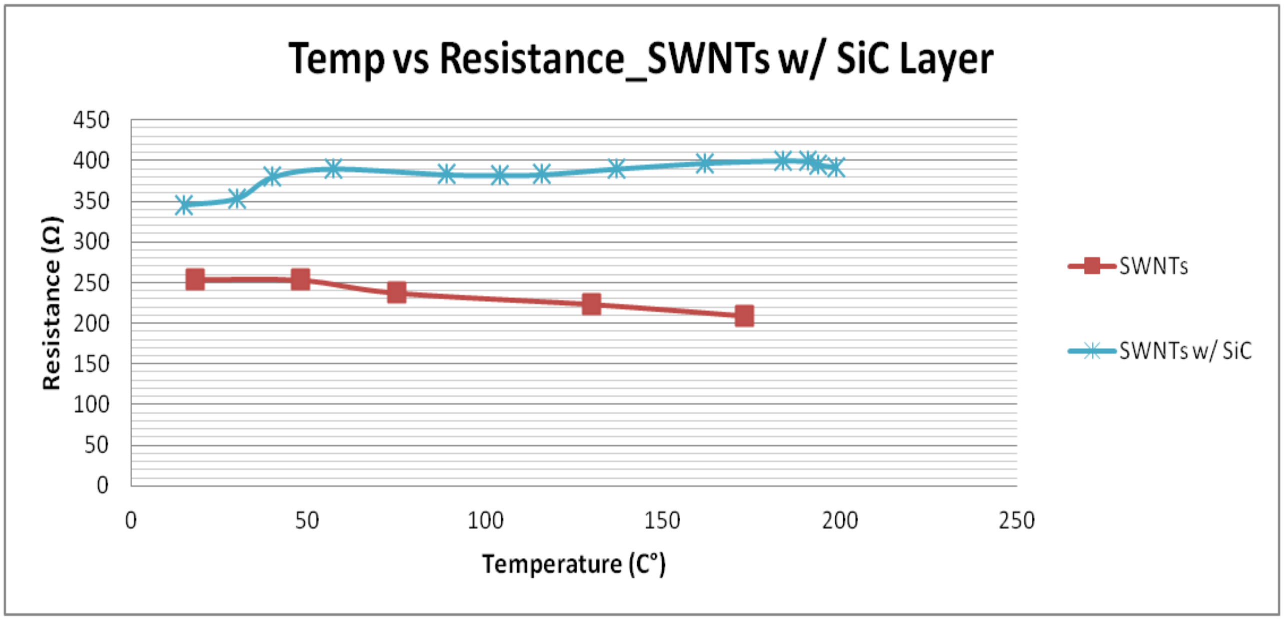

Figure 5.12: Resistance vs Temp, SWNTs vs SWNTs w/ a SiC top Layer

Figures 5.10, 5.11, & 5.12 reveal that SWNTs thermoelectric properties are slightly affected by the addition of a SiC layer. The addition of the SiC appear to intensify the film resistance and thus slightly reducing the current output. Note that Figure Y shows exactly the opposite, as it depicts current output actually slightly increased. This increase however is due to measurement discrepancy, and in this particular test scenario, the resistance result provide a more precise representation.

5.1.5 Thermoelectric Measurements Comparison Between MWNTs and MWNTs w/ SiC Layer

Figures 5.13, 5.14, & 5.15 contrast the thermoelectric properties of MWNTs vs MWNTs with an SiC layer.

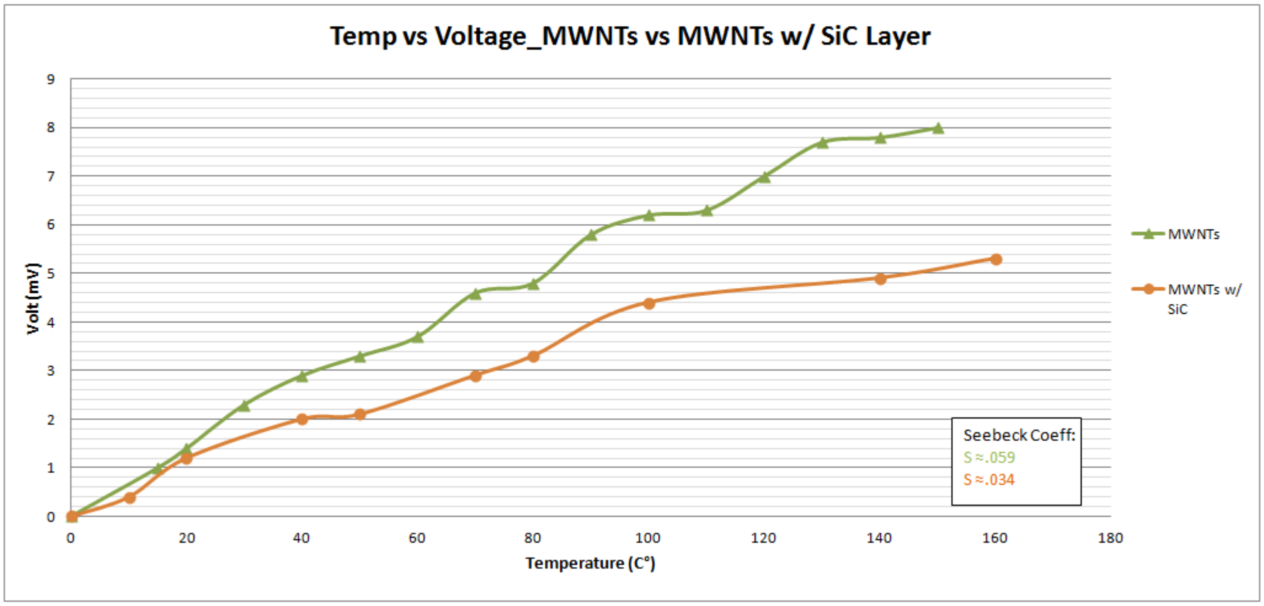

Figure 5.13: Voltage vs Temp, MWNTs vs MWNTs w/ a SiC top Layer

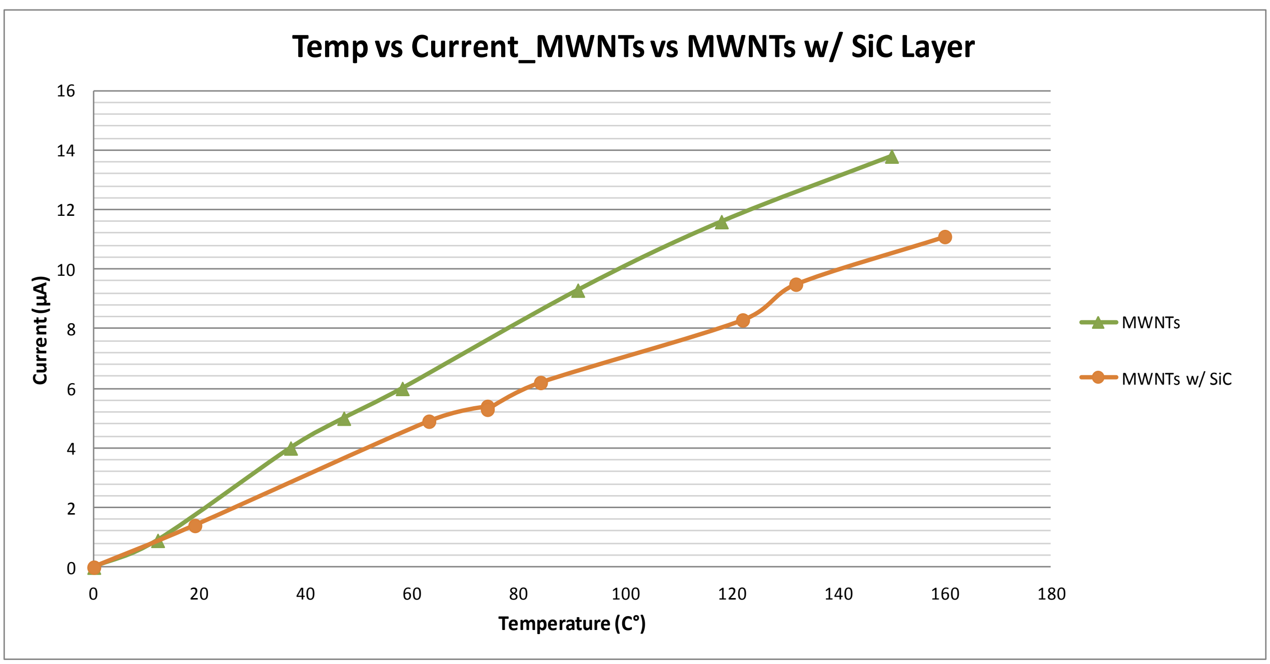

Figure 5.14: Current vs Temp, MWNTs vs MWNTs w/ a SiC top Layer

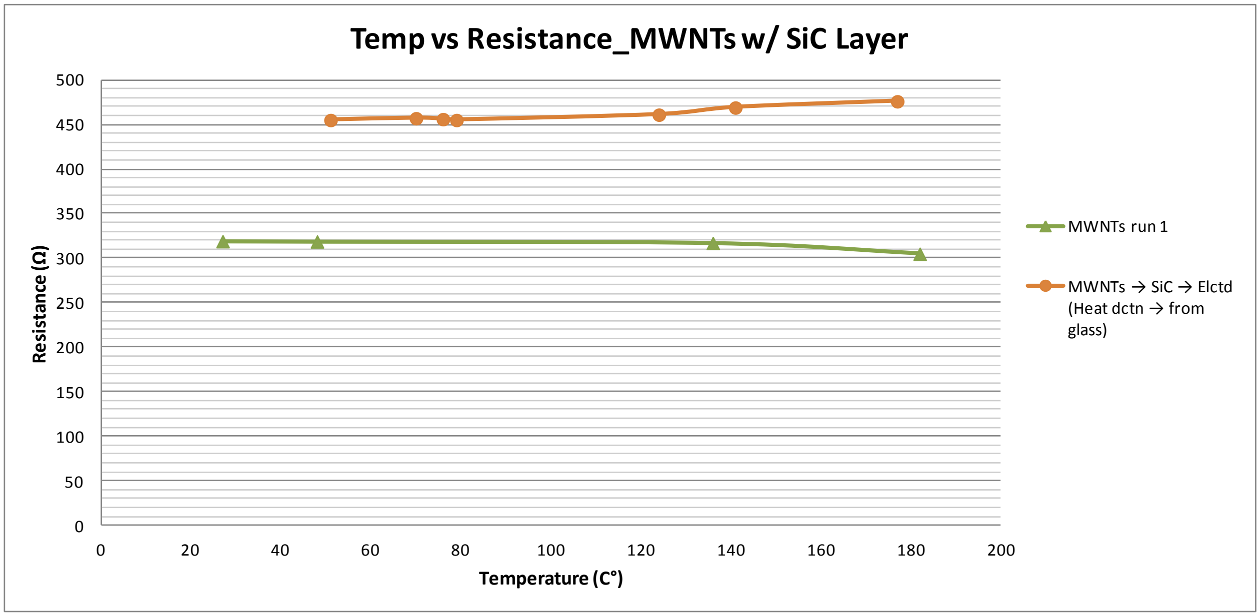

Figure 5.15: Resistance vs Temp, MWNTs vs MWNTs w/ a SiC top Layer

Figures 5.13, 5.14, & 5.15 reveal that MWNTs thermoelectric properties are greatly affected by the addition of an SiC layer. The addition of the SiC layer appears to intensify the film resistance roughly 68 %, and conversely reduces the electrical current output. Note how Current and Resistance results agree as one increases and the other decreases. This hypothesis is also supported by the voltage vs temperature results, as these illustrate that both voltage and the seebeck coefficient dropped with the addition an of an SiC layer.

5.1.6 Thermoelectric Measurements of Isolated SiC Nanoparticle Layer

Figures 5.16, 5.17, 5.18 reveal the thermoelectric properties of SiC nanoparticles alone. The outcome for every case resulted in zero, which suggests that SiC is not thermoelectric.

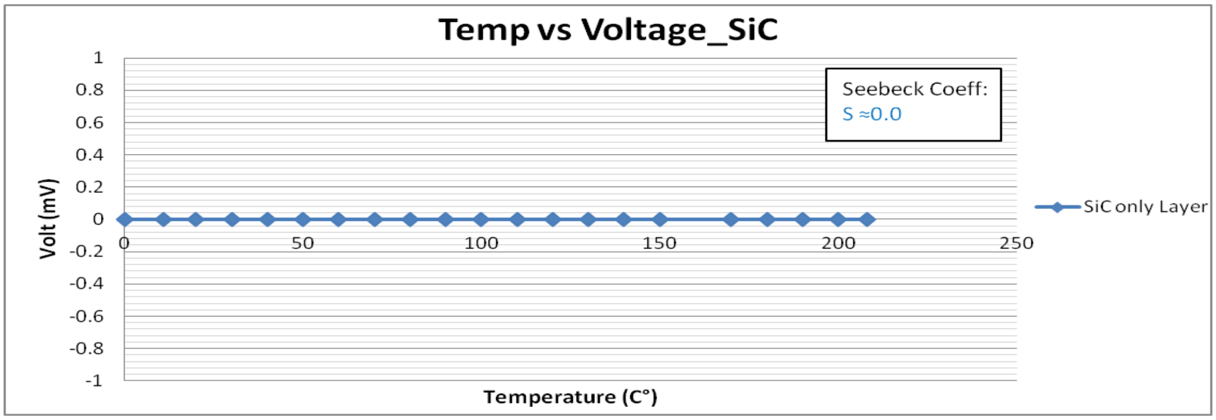

Figure 5.16: Voltage vs Temp, Isolated SiC layer

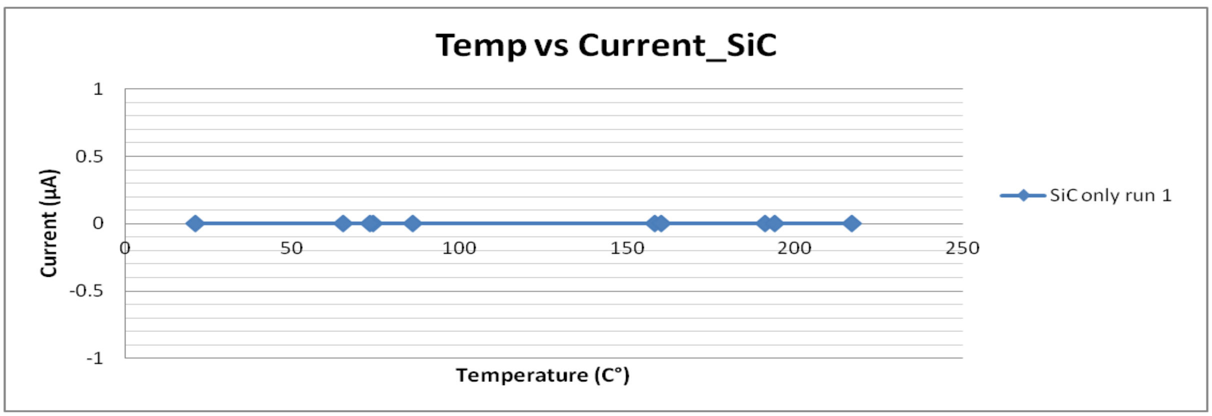

Figure 5.17: Current vs Temp, Isolated SiC layer

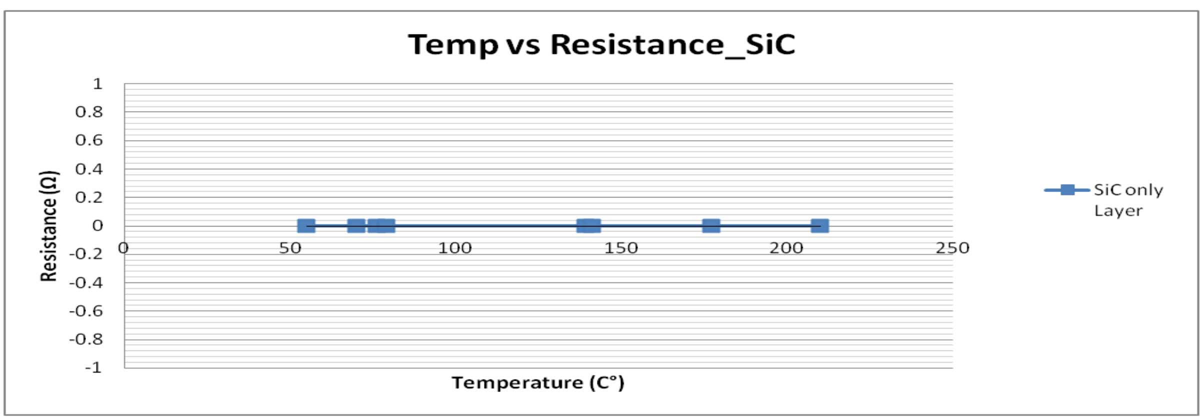

Figure 5.18: Resistance vs Temp, Isolated SiC layer

5.1.7 Thermoelectric Measurements of Electrode Contact emplacement relative to nanolayer

There was trivial thought that on the experiment "Thermoelectric Contrast of SWNTS vs SWNT w/ SiC layer", the electrode (solder) could have been making direct contact with the CNT layer, despite SiC sat in between. Suspicion arouse from the idea that the SiC layer may not have thoroughly cover the CNT film, or the SiC layer could have been porous, allowing the electrode to make contact with the CNT layer. This would then explain why there were no major differences between individual SWNTs and SWNTs with an SiC layer. Therefore, samples were prepared and thermoelectric measurements were performed with special care to determine if there were significant differences between the electrode making contact only with the uppermost SiC layer, versus making contact with both the CNT and SiC layers. A measurement was also performed to test thermoelectricity effects based on the direction of the heat.

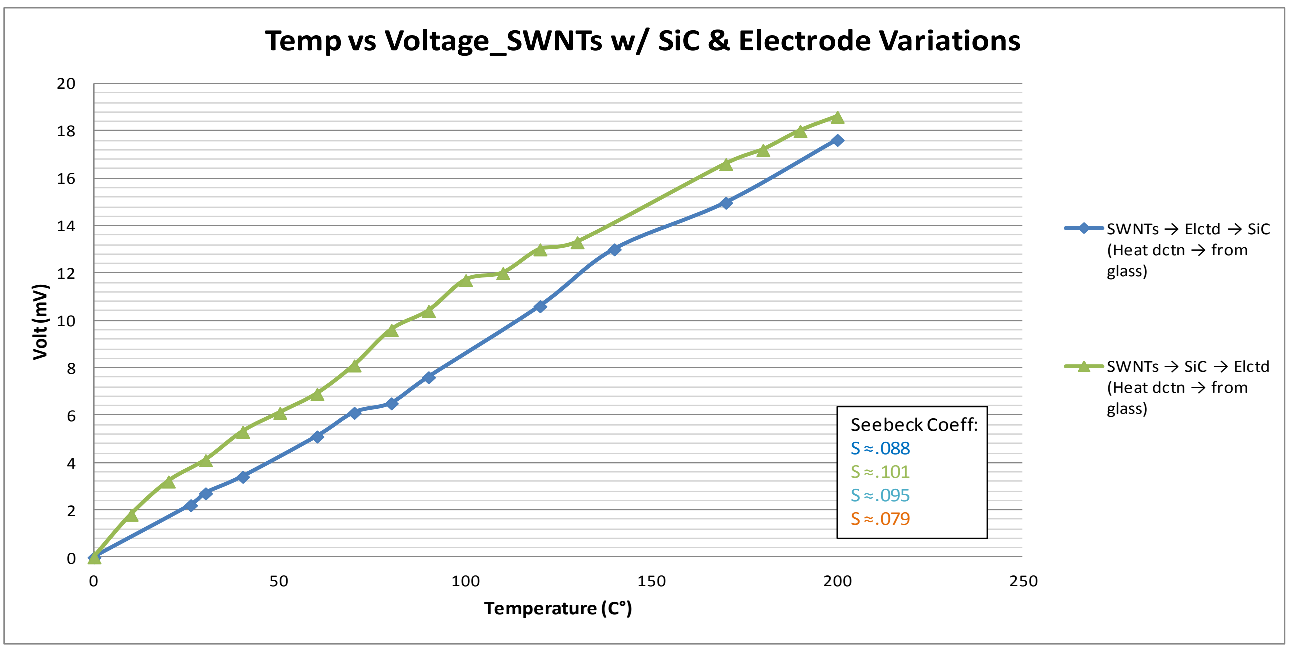

Figure 5.19: Voltage vs Temp. Electrode Contact to Respective Layer

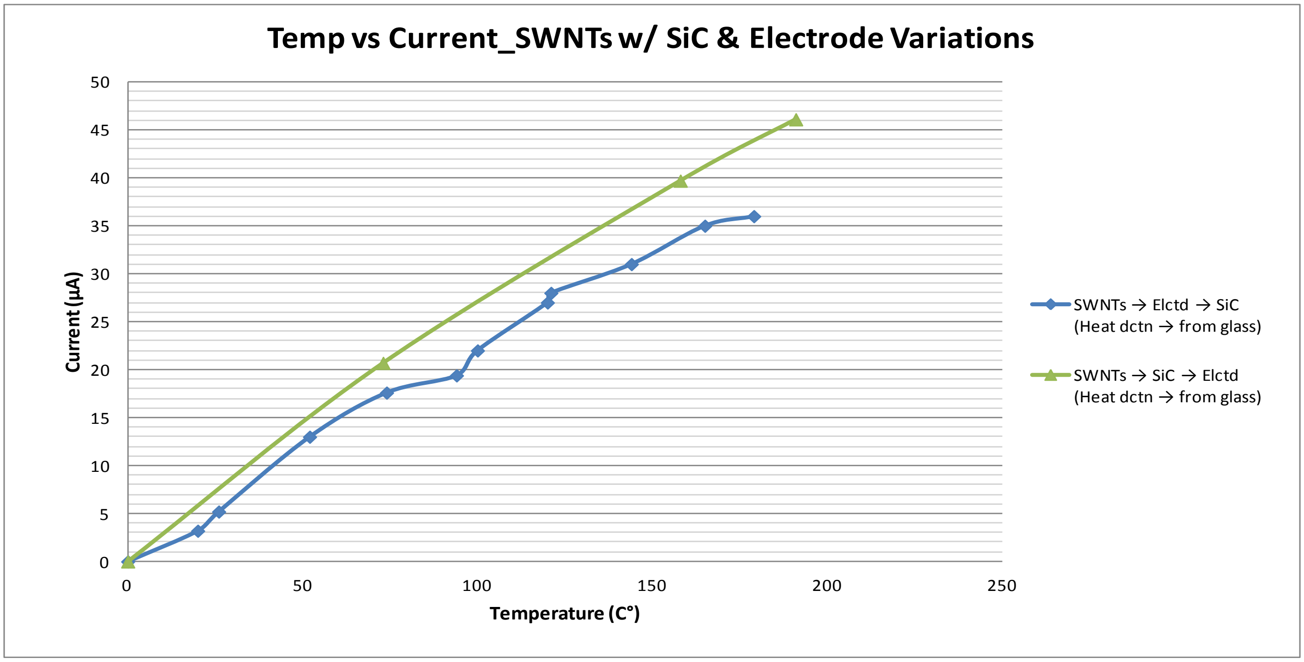

Figure 5.20: Voltage vs Temp. Electrode Contact to Respective Layer

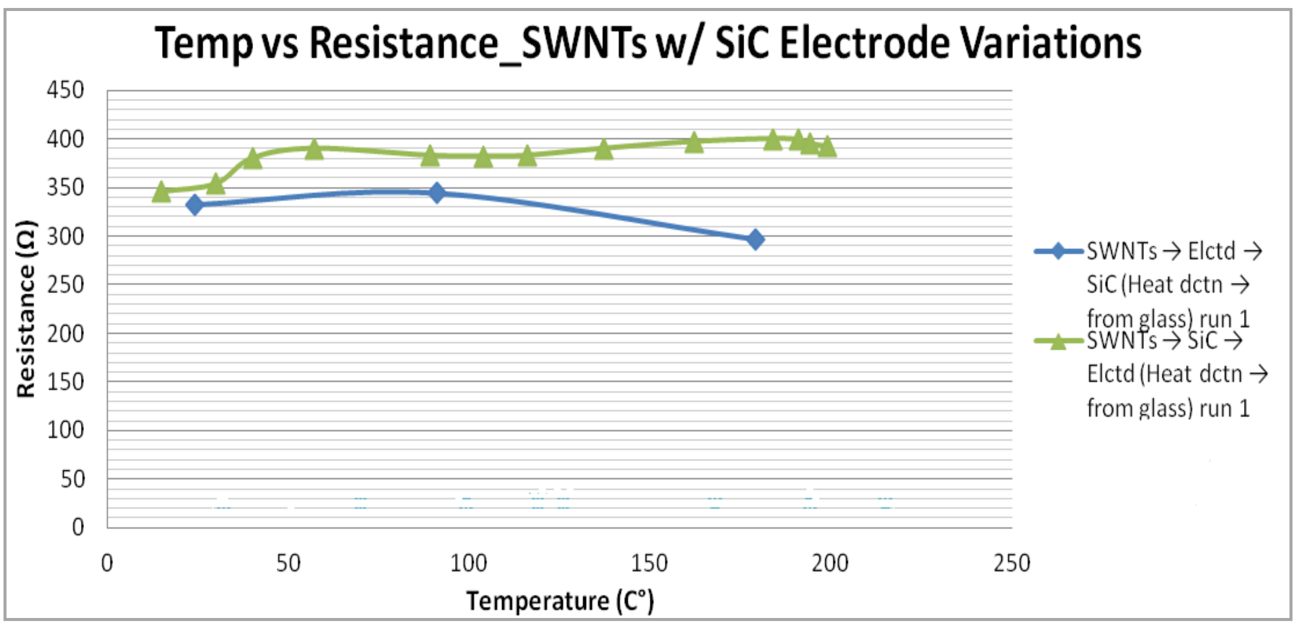

Figure 5.21: Voltage vs Temp. Electrode Contact to Respective Layer

Figures 5.19, 5.20, & 5.21 confirm thermoelectric results are equivalent and unaffected by the respective nanoparticle layer making direct contact with the electrode, and neither does the direction of the heat source affect the results. This is due to the relatively small thickness of the nanoparticle

coatings, which allows layers to overlaps such there is direct contact between the electrode and conductive CNT film.

5.1.8 Thermoelectric Measurement Comparisons between SWCNTs w/ SiC Layer and SWNTS/SiC Nanoparticle Mixtures at Varied Concentrations.

Figures 5.22, 5.23, & 5.24 illustrate a comparative analysis of the thermoelectric repercussions of the pre-mixture of SiC nanoparticles and CNTs nanoparticles in contrast to a simple SiC layered CNT film. Thermoelectric results reveal SiC and CNTs pre-mixed films degrade the generation of electrical current in comparison to SiC layerd CNT films. Moreover, higher SiC concentrations lead to lower current generation. The voltage potential generated is un-affected.

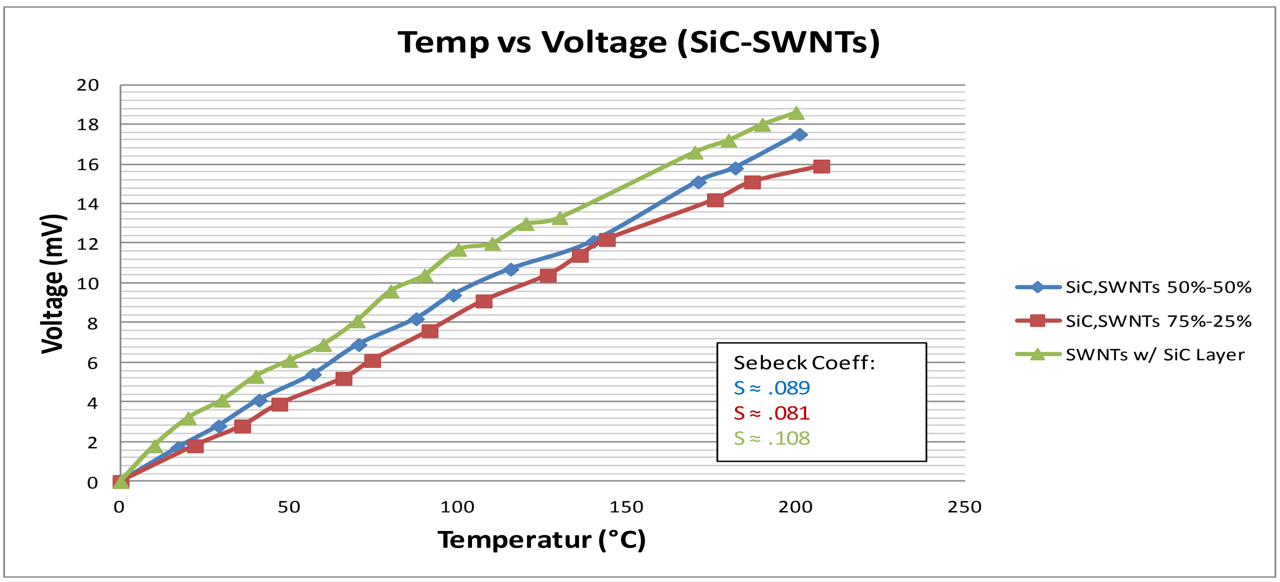

Figure 5.22: Voltage vs Temp. Pr-Mixed SiC and CNT nanoparticles vs SiC Layered CNTs

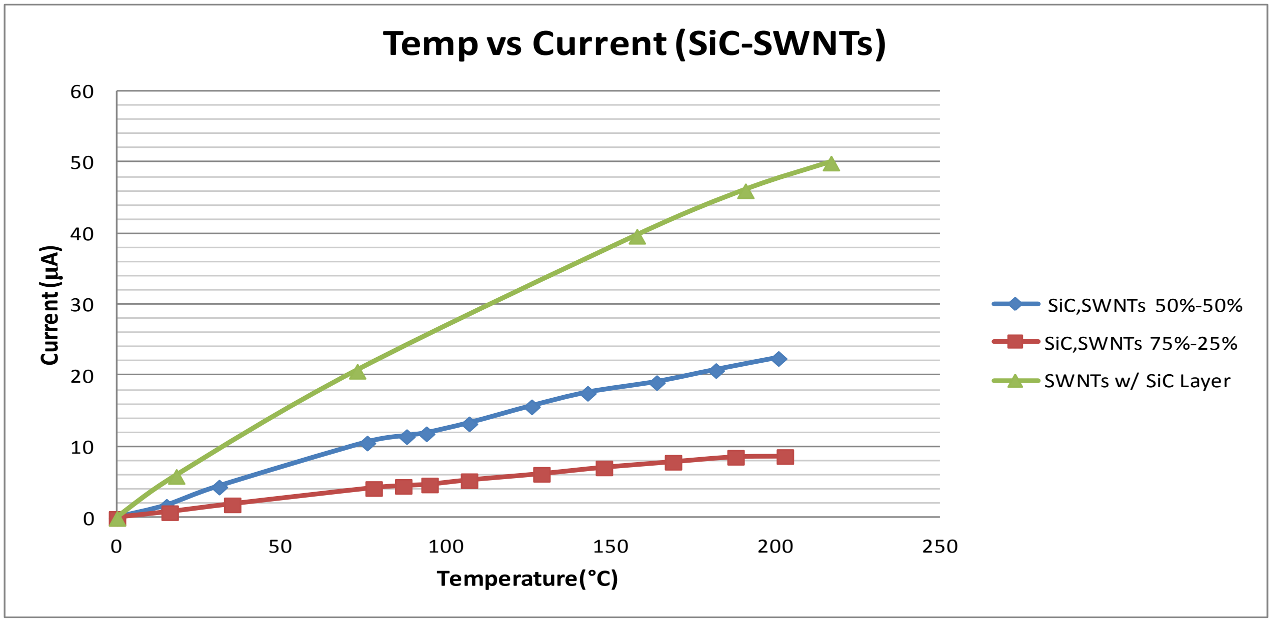

Figure 5.23: Current vs Temp. Pr-Mixed SiC and CNT nanoparticles vs SiC Layered CNTs

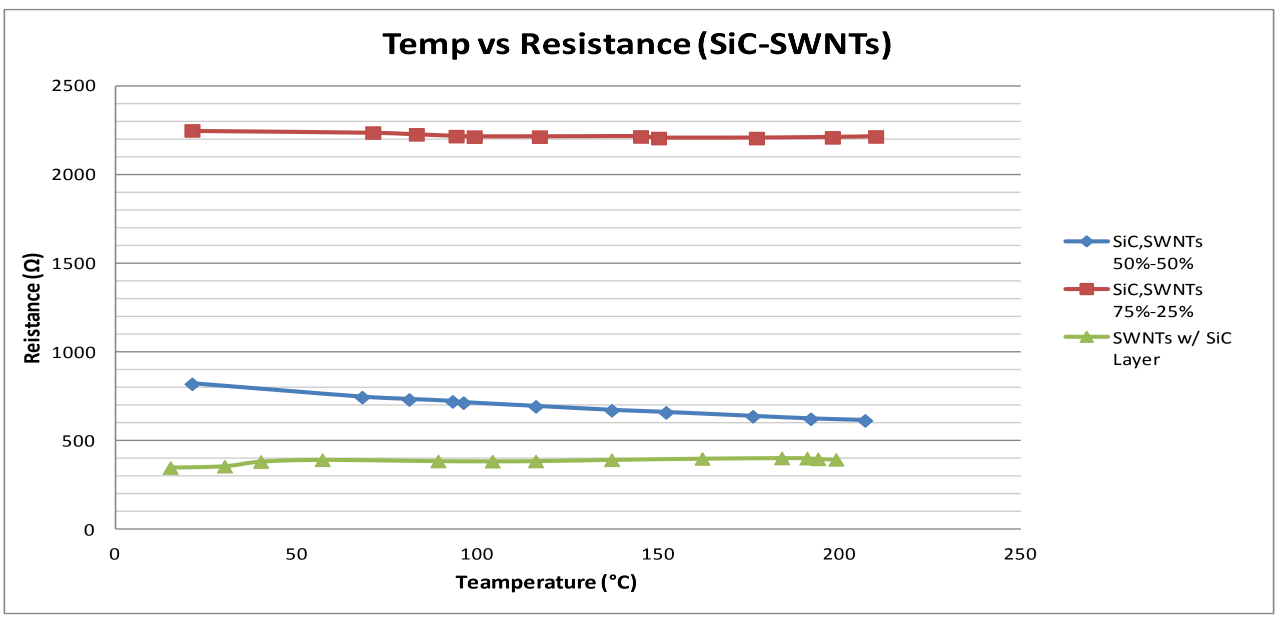

Figure 5.24: Resistance vs Temp. Pr-Mixed SiC and CNT nanoparticles vs SiC Layered CNTs

Chapter 6.0: Conclusion and Future Work

5.1 Conclusion

It is concluded that carbon nanotube films as an adjoining conductive material with a dissimilar metal (e.g. alumel) offer and/or enhance thermoelectric behavior, and presents itself as a linear function. Results suggest that the random distribution of nanotubes does not affect thermoelectric behavior provided the setup is analogous to that of thermoelectricity in thermocouples. High purity SWNTs present thermoelectric properties twice the magnitude of the MWNT counterpart. It was realized that pristine silicon carbide is non-conductive, hence not thermoelectric. The inclusion of silicon carbide nanoparticles both as a layer and as a pre-mixed compound with CNTs, introduce film resistance which in turn degrade electrical current. The incorporation of SiC however, does not significantly demean the thermoelectric properties; in which case, the thermoelectric properties can yet be advantageous based on its application.

5.1 Future Work

Although this study concentrated on the thermoelectric study of isolated CNTs and SiC nanoparticles, this project provided a foundation in thermoelectric behavior. CNTs and SiC nanoparticles have been profoundly explored by third parties, in their inclusion into ceramic composites and alloys. Thus, this project propose future work potential for further thermoelectric exploration, now tentatively in the composite and/or alloy field of study.

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Vita

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