Enhanced Metal Contacts to Carbon Nanotube Networks through Chemical and Physical Modification

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Enhanced Metal Contacts to Carbon Nanotube Networks through Chemical and Physical Modification

by

Nathanael David Cox

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctorate of Philosophy in Microsystems Engineering

Microsystems Engineering Program
Kate Gleason College of Engineering

Rochester Institute of Technology
Rochester, New York
27 July 2016
Enhanced Metal Contacts to Carbon Nanotube Networks through Chemical and Physical Modification
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ABSTRACT

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Dissertation Title: Enhanced Metal Contacts to Carbon Nanotube Networks through Chemical and Physical Modification

Carbon nanotubes (CNTs) are an emerging class of nano-structured carbon materials which are currently being studied for applications which would benefit from their desirable electrical and mechanical properties. Potential benefits such as improved current density, flexure tolerance, weight savings, and even radiation tolerance have led to their implementation into numerous devices and structures, many of which are slated for use in space environments. The role of CNTs can be quite diverse, with varied CNT electronic-types and morphologies dictated by the specific application. Despite numerous CNT types and morphologies employed by these technologies, a common link between nearly all of these devices and structures is metal contact to CNTs, where the metal components often provide the link between the carbon nanotubes and the external system.

In this work, a variety of CNT-metal systems were characterized in terms of metal morphology analysis and CNT-metal electrical and mechanical interactions, in response to chemical and structural modifications. A large portion of the work additionally focuses on ion irradiation environments. A diverse number of experiments related to CNT-metal interactions will be discussed. For instance, electrochemical interactions between ion-irradiated single-wall CNTs (SWCNTs) and metal salt solutions were utilized to selectively deposit Au nanoparticles (Au-NPs) onto the SWCNTs. A direct correlation was established between defect density and Au-NP areal density, resulting in a method for rapid spatial profiling of ion-irradiation induced defects in SWCNTs. The effect of ion irradiation on the CNT-metal interface was also investigated and it was found that the contact resistance of Ag-SWCNT structures increases, while the specific contact resistance decreases. The increase in overall contact resistance was attributed to increased series resistance in the system due to damage of the bulk SWCNT films, while the decrease in specific contact resistance was attributed to Ag atoms being forward-scattered into the top 5 nm of SWCNT film, as revealed by computational simulations. Additionally, development of Ag-CNT metal matrix composite (MMC) thin films for advanced space solar cell electrodes is discussed. SWCNTs and multi-walled CNTs (MWCNTs) were utilized as reinforcement material in Ag electrodes to address problems related to micro-cracks causing electrode fracture and loss of power in solar cells. A method for creating free standing films was developed to enable mechanical property characterization of the MMCs, and it was found that SWCNTs significantly increase the toughness of Ag thin films, due to the SWCNT tensile strength and strain capabilities. CNT-MMC grid-finger structures were also fabricated by solar cell process-compatible techniques and subjected to electrical testing under mechanical stress. The results showed that CNTs are capable of spanning gaps in Ag electrodes upon fracture, both electrically and mechanically.
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1 Introduction

The unique nanoscale structure of carbon nanotubes (CNTs) results in many incredible material properties such as high current density[1], ballistic conduction[2, 3], radiation stability[4, 5], high thermal conductivity[6], and high tensile strength[7], which often exceed those of traditional bulk-scale materials. CNTs can also exhibit metallic, semi-metallic, and semiconducting behavior, with a wide range of band-gaps[8-12]. These unique physical properties have driven research toward implementing CNTs into a wide array of devices and structures, including, but not limited to, field effect transistors[13, 14], thin film transistors[15, 16], transparent conductive electrodes[17, 18], flexible electronics, and wires and cables[19, 20]. The numerous CNT-based applications which are being investigated span from nano- to macro-scale, and utilize a wide range of CNT types and form factors. A majority of these structures share one commonality: metal contacts to the CNTs are often required to connect the CNTs to external parts and electrical circuits. Thus, understanding of the physical interactions between CNTs and metals, and the characterization of the electrical and mechanical properties of various CNT-metal systems is extremely important for progress toward implementation and commercialization of CNT-based applications.

The following sections (Chapters 1.1 – 1.3) provide some of the fundamental properties and observations to-date for CNTs, CNT-networks, and metal interactions with CNT networks. This general background information is followed by a more focused
discussion in Chapter 1.4 on the topic of space environments and potential issues which may affect CNT-metal networks utilized in space exploration.

1.1 Carbon Nanotube Fundamentals

Carbon nanotubes are cylinders of hexagonally bonded carbon atoms with nanometer diameters. CNTs can be either single or multi-walled (SWCNTs and MWCNTs, respectively), where MWCNTs have several concentric SWCNTs with different diameters, nested within one another. The CNT crystal structure is based on graphene, a hexagonal sheet of sp²-bonded carbon atoms, an illustration of which is shown in Figure 1. The graphene basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are at an angle of 60° and have magnitude of 2.461 Å. The SWCNT crystal structure is described by a sheet of graphene rolled into a seamless cylinder with a circumference equal to the sum of integer multiples of the basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. In other words, a vector $n\mathbf{a}_1 + m\mathbf{a}_2$, also known as the chiral vector, is the direction in which the nanotube is rolled its magnitude is the SWCNT circumference. The integers “n” and “m” which describe the resulting SWCNT are the chiral indices, usually denoted as (n,m). An example of the chiral vector corresponding to an (8,3) SWCNT is shown in Figure 1. The cylindrical symmetry of CNTs makes it possible to estimate many of the properties of CNTs by relation to the chiral indices.
There are numerous ways in which a sheet can be rolled into a cylinder, resulting in many different chiral vectors, which ultimately determines the crystal structure and the diameter. Due to the diverse crystal structures possible, many interesting spectroscopic, mechanical, and electrical properties emerge. For instance, the SWCNT electronic type (semiconducting or metallic) can be described by the chiral indices. The different possible combinations of chiral indices determine that 1/3 of SWCNTs are metallic, a purely statistical result. This type of distribution is observed in CNTs produced by laser ablation, arc discharge, and HiPCO processes. Metallic SWCNTs (M-SWCNTs) result when $n - m = 3p$, where $p$ is an integer. All other SWCNTs are semiconducting (S-SWCNTs) with varying band-gaps. The SWCNT diameter essentially defines the zone boundary through 1D quantum confinement, and the crystal structure determines how
the wave vector overlaps with the zone boundaries in reciprocal space[21]. Thus the band-gap is strongly dependent on SWCNT diameter, a theoretical approximation of which is $E_g \sim 0.8 \, eV/d$, where $d$ is the diameter. Experimentally, $E_g$ has been shown to be as high as $\sim 1.1 \, eV/d$, or as low as $\sim 0.70 \, eV/d$[22-24].

Although carbon nanotubes can be described as graphene sheets rolled into cylinders, the actual CNT formation occurs from condensation of carbon atoms into nanotube structures under specific synthesis conditions. The three most common techniques for SWCNTs synthesis are chemical vapor deposition (CVD), arc-discharge, and laser vaporization, each with inherent advantages and disadvantages. These processes can be categorized by synthesis temperatures and carbon feedstock. For instance, arc techniques employ the highest temperatures (>2000 °C), followed by laser vaporization (1000 °C – 1200 °C), followed by CVD (Room temp – 1200 °C). The carbon feedstock for arc discharge and laser vaporization is solid carbon (graphite), while CVD obtains carbon from gas phase precursors (methane, acetylene, etc.) MWCNTs and SWCNTs can be synthesized by any of these methods; however, for SWCNT synthesis, catalyst particles are required. For CVD processes, the catalyst particles are formed from the gas phase or pre-deposited on the substrate, while for arc and laser synthesis, they are typically embedded in the graphite pre-synthesis. These catalysts are often micro- or nanoparticles composed of elements like Ni, Co, and Fe, but many others have been used as well[25].

CVD offers high throughput and the added benefit of direct growth on a variety of substrates. Localized growth can be achieved by lithography, and straight, directionally
oriented SWCNTs can be aligned in the direction of gas flow or as a vertically oriented “forest”. Moreover, precise control of the various synthesis parameters can be utilized to achieve tighter distributions of chiralities or diameters, which is useful from a device perspective because of the influence of SWCNT structure on electronic properties. The SWCNTs produced by CVD, however, are more prone to defects and may have lower crystalline quality than SWCNTs produced by arc or laser techniques. Another drawback is that for CNTs grown on device substrates, removal of catalysts and impurities can be difficult[26].

Arc and laser techniques can both produce large yields of SWCNTs with high crystalline quality. The disadvantages of these techniques are less control of the SWCNT properties, and the resulting soot contains amorphous carbon and catalyst particles, which require additional processing for SWCNT isolation[27]. Additionally, solution processing is required to transfer to substrates for many device applications, which can introduce unwanted molecules into the fabrication process.

The use of SWCNTs in devices may require very pure or defect-free samples depending on the application, as the material properties will be altered by the presence of impurities such as amorphous carbon or residual metal catalysts. There are purification methods to remove such impurities, including various heat treatments to oxidize impurities, and chemical treatment by acids, usually acid reflux techniques, to remove unwanted carbonaceous impurities and catalyst particles[28]. However, chemical and heat treatments can also introduce defects into the system by oxidizing or functionalizing the SWCNTs, creating vacancies or dangling bonds on the side-walls which change the
absorption properties, are more chemically reactive, and act as scattering sites[29]. Contrary to other material systems, even very small defect concentrations can be detrimental for certain applications. For instance, in Si-based devices, low concentrations of impurities or crystal defects cause scattering or trapped charges, but electrostatic screening effects negate any significant impact of these scattering sites on device performance. However, charge carriers in 1-D systems such as single SWCNT FETs cannot avoid scattering from a defect site, making the presence of defects much more significant[30]. On the other hand, for a bulk CNT-metal composite, where the SWCNTs are intended for mechanical support and redundant conduction paths, the presence of defects may be much more tolerable. Hence, the intended device applications will strongly affect the choice of processing, purification, and synthesis conditions.

Separation of SWCNTs by structural or electronic properties is another type of post synthesis processing that may be necessary depending on the application. For instance, S-SWCNTs are implemented as a semiconductor replacement in transistors and similar applications, and the presence of even a small number of M-SWCNTs can cause leakage currents and inhibit gate control in these devices. These device performance issues have been a major driver for development of scalable separations techniques, because these technologies require a high degree of uniformity and precise control of electronic properties for a reliable performance. Phase pure SWCNTs are typically referred to as enriched, and significant progress has been made toward production of electronic type-enriched, diameter-enriched, and even chirality-enriched (or mono-chiral) SWCNT samples. Separations techniques range from selective growth, destruction, or chemistry, to column chromatography, ultracentrifugation, or polymer dispersions[8, 12, 31-34].
Though progress has been made toward selective growth of enriched SWCNT samples by controlling growth conditions, post-synthetic techniques are more efficient and scalable\[10\]. It is important to note that the cost and processing time increase dramatically with the level of enrichment attained.

1.2 Electrical Transport in CNT-Metal Networks

Many factors affect the measured resistance of a CNT network, such as the network density, CNT type \((i.e., \text{MWCNT or SWCNT})\), and the relative enrichment of electronic types \((i.e., \text{ratio of S-SWCNT to M-SWCNTs})\). Thus, the transport properties of CNT networks can be a very complex issue. Figure 2 is a graphical representation of the cross section of a typical SWCNT thin film structure which will be used to highlight and explain some of the factors that contribute to the overall transport properties of SWCNT networks. The structure represents a common SWCNT film on semi-insulator (e.g. Si/SiO\(_2\)) architecture, such as thin film transistors or on-chip resistors. The SWCNT thin film (Region II) represents a mixed electronic type thin film, with an S-SWCNT (red) to M-SWCNT (green) ratio of 2:1. The metal contacts (M1 and M2) to the SWCNT thin film are also shown (Region I).
Figure 2. Schematic showing a cross-sectional view of a typical SWCNT network. Region I is the bulk thin film and region II is the metal contacts to the SWCNT network. The thin film is composed of individual S-SWCNTs and M-SWCNTs, and examples of each are labeled in region I as (a) and (e), respectively. The three major types of SWCNT junctions are labeled in region I as (b) S-S junction, (c) S-M junction, and (d) M-M junction.

The overall resistance of a CNT network such as that in Figure 2 is governed by the resistances of the bulk CNT film ($R_{bulk}$), the metal contacts ($M_1$ and $M_2$), and the CNT-metal interface ($R_{C1}$ and $R_{C2}$). As charge carriers are transported into one metal contact, through the film, and collected at the alternate contact, the network can be thought of as the series sum of these resistances, or

$$R_{total} = R_{M1} + R_{C1} + R_{Bulk} + R_{M2} + R_{C2}$$  \hspace{1cm} (1)

where resistance between the metals and external connections (i.e. wires) is considered negligible. The resistances of the bulk thin film and the SWCNT/metal contacts are in turn affected by both the network morphology and individual properties of the CNTs and metals. As such, a thorough understanding of each constituent part of the network is necessary for understanding their impact on the resistance of the system as a whole.
1.2.1 CNT Network Transport

Beginning with the resistance of the bulk film (Figure 2, Region II), a SWCNT network can be thought of as a circuit with many parallel conduction paths, each path composed of individual resistors (either SWCNTs or bundles) in series. The intrinsic resistance of each individual SWCNT \( R_{\text{CNT}} \) and resistance associated with charge transport barriers at the SWCNT junctions \( R_J \) will contribute to the resistance along a given path, as illustrated in Figure 3. The resistance of each conduction path is then the sum of \( R_{\text{CNT}} \) and \( R_J \).

\[
R_{\text{path}} = \Sigma R_{\text{CNT}} + \Sigma R_J
\]  

(2)

At the individual level, the band structure and quantum confined nature of M-SWCNTs make 1-D ballistic transport possible, and has been observed experimentally\[3, 35, 36\]. Ballistic transport is a quantum mechanical phenomenon that occurs when the mean free path \( l_{\text{mfp}} \) of charge carriers is very long, resulting in essentially no scattering of charge carriers. This can be expressed in terms of an ideal resistance for a SWCNT, sometimes called the quantum resistance, as\[37\]

\[
R_Q = \frac{h}{2e^2M}
\]  

(3)

where \( h \) is Planck’s constant, \( e \) the charge of an electron, and \( M \) the number of conduction modes in a channel, which is 2 for nanotubes. The quantum resistance, \( R_Q \)
Figure 3. Schematic illustrating the sources of resistance along a conduction path in a SWCNT network, with the intrinsic resistance ($R_{\text{CNT}}$) of an individual SWCNT and the junction resistance ($R_J$) between SWCNTs shown.

corresponds to a resistance value of $R_Q \approx 6.5 \, k\Omega$[3]. Though early examples of ballistic transport were to M-SWCNTs, under appropriate gate voltage conditions and with improvements in metal contacts, S-SWCNTs[2, 35, 38] and even small SWCNT bundles[36] also exhibited quantum resistance. In one instance Li et al.[35] measured ballistic transport in both M- and S-SWCNTs, and suggested a standard resistance per unit length ($R/L$) of ~6 $k\Omega/\mu$m for nanotubes, supported by data from several publications. This would correspond to a mean free path for electrons of ~1.1 $\mu$m. However, reported values for both ($R/L$) and $l_{\text{mfp}}$ have varied. For instance, one article reported an $R/L$ value of 10 $k\Omega/\mu$m for S-SWCNTs[36], and another reported a $l_{\text{mfp}}$ value of 2.9 $\mu$m[38]. These variations can be understood by changes in the mean free path for
charge carriers, as transport in 1-D systems is strongly affected by scattering from defects or phonon modes. Therefore, the resistance of an individual nanotube may be expressed more accurately as \[39, 40\]

\[ R_{CNT}(L) = \frac{h}{4e^2} \left( \frac{L}{l_{mfp}} + 1 \right) \]

where \(l_{mfp}\) is variable with temperature. Strong evidence has been shown that M-SWCNTs have a much higher \(l_{mfp}\) than S-SWCNTs, but the measured values can vary even between samples from the same synthesis conditions with the same electronic type, due to random defect distributions [40]. Thus, quantum resistance is a theoretical limit, but practically other factors will influence \(R_{CNT}\).

Another consideration for \(R_{CNT}\) is that SWCNT networks very often are composed of SWCNT bundles rather than individual SWCNTs. Although ballistic transport has been observed in small bundles, SWCNT bundles typically have higher resistance than single SWCNTs. For instance, the highest measured conductivity for a small SWCNT bundle was \(3 \times 10^6\) S/m, while values of \(7 \times 10^7\) S/m have been measured for individual SWCNTs [19]. It has been suggested that the increase in bundle resistance as compared to individual SWCNT resistance may be due to inter-tube scattering [41].

Charge transport barriers at nanotube junctions (\(R_J\) in Figure 3) are the other major contribution to the resistance along a given conduction path and has been suggested to be the dominant source of resistance in a CNT network. Several works on this topic investigated the junction resistance of individual SWCNTs and small bundles, primarily utilizing conductance atomic force (or scanning probe) microscopy (C-AFM) to
determine transport properties and create current maps of the networks[9, 42-45]. The results of these studies overwhelmingly showed that there are increases in resistance at junctions. However, the relative magnitude of $R_J$ has been shown to be strongly dependent on the electronic type and also bundle size of the SWCNTs[45].

The three main types of junctions that occur in a CNT network are metallic to metallic (M-M), semiconducting to semiconducting (S-S), and metallic to semiconducting (M-S). An early investigation into $R_J$ using source/drain contacts in different configurations measured an M-M junction resistance ($R_{M-M}$) of 608 kΩ, while rectifying behavior was observed for an M-S junction, with $R_{M-S} > 250$ GΩ at zero bias[46]. It was suggested that there was a thin tunneling barrier at the M-M junction, while a possible combination of Schottky barriers and tunneling barriers occurred at the M-S junction. Schottky and tunnel barriers arise from misalignments in the Fermi levels and specific bands from nanotube to nanotube, and will be covered in more detail in a following section. A C-AFM study on $R_J$ as a function of SWCNT electronic-type revealed that at $R_{M-M}$ was $\sim 200$ kΩ, on the order of the resistances of the individual SWCNTs, with a tunneling transmission probability of 2%-6% at the junction, while S-S junction values were found to be $\sim 400$ to 2100 kΩ. In contrast, at M-S junctions, $R_{M-S}$ was over two orders of magnitude greater, than $R_{M-M}$ or $R_{S-S}$, with a tunneling transmission probability of only 0.02% and Schottky barrier energies of 100 to 300 meV[9]. This trend of $R_{M-M} < R_{S-S} \ll R_{M-S}$ has been observed in other work[42, 44, 46], with additional evidence that at the S-S junctions, $R_{S-S}$ can be modified by appropriate gate voltages[44],
SWCNT bundling can also have an impact on the $R_J$, and consequently, on the resistance of the network. Systematic studies done by Nirmalraj et al.[45], showed the impact of SWCNT bundles on $R_J$, where many sparse networks were analyzed by C-AFM. Bundle diameters were categorized as single (no bundling), small (2.5 – 4.5 nm), medium (4.5 – 7 nm), or large (7 – 14 nm), and $R_J$ values were measured over many samples. The average $R_J$ values from single, small, medium, and large were 98 kΩ, 230 kΩ, 294 kΩ, and 2.677 MΩ, respectively. It was suggested that the $R_J$ being measured may actually be due to both charge transport from bundle to bundle, as well as charge transport within a bundle. Regardless of the mechanism, the evidence suggests that thoroughly dispersing SWCNTs before network fabrication can decrease the resistivity of the network by decreasing $R_J$.

Many authors have concluded that $R_J$ is the primary source of resistance along a given conduction path and therefore, for the network as a whole. Although current evidence strongly suggests that this is the case, the contribution of $R_J$ to $R_{bulk}$ cannot be assumed to completely overshadow contributions from $R_{CNT}$ for all networks. The studies regarding $R_J$ were often conducted on very straight, pristine samples grown on the substrates, where the mean free path is long, and $R_{CNT}$ is very low. The mean free path in SWCNTs, however, can vary depending on synthesis, curvature of the SWCNTs, and even substrate effects. For network fabrication, the SWCNTs are often subjected to acid purification, thermal oxidation, and ultrasonicated into surfactant dispersions. The effects of this processing can be to dramatically reduce the mean free path by introducing defects[47]. Additionally, recent advances in separations have enabled more electronically phase pure films, and a majority of the junctions in these films will be
homogeneous. Therefore, the impact of \( R_J \) on the measured network resistance will certainly change relative to \( R_{\text{CNT}} \), depending on the processing, synthesis conditions, and relative enrichment of electronic types present in the network.

Clearly there are many factors that affect both the intrinsic SWCNT resistance \( R_{\text{CNT}} \) and junction resistance \( R_J \). The overall network resistance \( R_{\text{bulk}} \) is determined by the parallel conduction paths in a given network with a nearly endless number of configurations; consequently, a single expression for \( R_{\text{path}} \) and \( R_{\text{bulk}} \) is not possible. Moreover, mapping the current through even moderately dense networks it is not practical, as has been done in a few cases for sparse networks. However, understanding these aspects at the individual level can provide valuable insight into the macroscopic transport properties of a CNT network.

The most common technique for analyzing the macroscopic electrical transport in a CNT network is to analyze measured values pertaining to the network resistance \( R_{\text{bulk}} \), and compare to various transport models. Typically this process involves measuring the sheet resistance over a range of temperatures, and from this value calculating the resistivity or conductivity based on the network thickness. The macroscopic transport in a CNT network is affected by the intrinsic SWCNT resistances \( R_{\text{CNT}} \) and the resistances of the junctions, and their impacts on the overall transport in the system can vary. For large junction resistances, the transport typically follows hopping conduction, while for smaller junction resistances, the transport can be described as metallic conduction interrupted by thin tunneling barriers. A discussion of both of these models is necessary for understanding the experimental observations of SWCNT network transport.
Hopping transport occurs in disordered systems, when spatially localized charge carriers “hop” to an unoccupied neighboring position. In disordered systems, the lack of long-range order creates single particle states, which are spatially “localized” and therefore should not contribute to conduction. However, phonons, photons, or electric fields can delocalize the charge carriers, enabling hopping transitions between localized states. Strong localization implies that the extent of the wave function is small, and the charge carrier has a low probability of transitioning to another state. There are different types of hopping conduction depending on the type of particle and the system. If, for instance, an electron hops to a more energetically favorable state, as opposed to simply the nearest neighbor, the transition is known as variable range hopping (VRH). Because VRH occurs by phonon assisted hopping or tunneling, at very low temperatures phonon motion is negligible, which should result in strong localization and near infinite resistivity (or zero conductivity)[48]. VRH transport can be described by Equation 5.

\[
\sigma(T) = \sigma_0 \exp \left[ -\left( \frac{T_0}{T} \right)^{\frac{1}{d+1}} \right] \quad (5)
\]

Here, \( \rho \) is the resistivity, \( T \) is temperature, \( d \) represents the transport dimensionality of the system, and \( T_0 \) is a characteristic temperature which can be determined by fitting. The significance of \( T_0 \) is that it is determined by the density of states at the Fermi level \( (N(E_F)) \) and the electron localization length \( (L_{loc}) \), or in terms of energy[41]

\[
k_B T_0 = \frac{16}{N(E_F)L_{loc}^3} \quad (6)
\]
where \( k_B \) is Boltzman’s constant. By equation 6, smaller \( L_{\text{loc}} \) values (stronger localization) will result in larger values of \( T_0 \), which will give a higher baseline resistivity regardless of the temperature. An idealized example of 2D-VRH transport is shown in Figure 4. Electrical conduction in SWCNT networks is often suggested to be related to VRH transport, which may be expected for networks where many highly resistive M-S junctions dominate, such as in sparse mixed networks.

As mentioned, another perspective for transport in SWCNT networks is related to metallic transport, since the SWCNTs (often) behave as ballistic conductors. However, even in purely M-SWCNT networks, the film cannot be considered as a simply a sheet of free charge carriers, because of the small tunneling barriers observed to be present at the junctions. Hence, the transport has also been described as fluctuation assisted tunneling (FAT) along with small contributions from phonon scattering along the individual SWCNTs. In the perspective of hopping transport, this is sometimes referred to as weak localization, where carriers are much more probable to transition to other states. Thus, even at low temperatures, charge carriers can still have a non-negligible probability of transitioning to a neighboring state, also called quantum tunneling. The model for this type of transport can be described by equation 7[49]

\[
\frac{1}{\rho(T)} = \sigma(T) = \left[ A \exp \left( -\frac{T_m}{T} \right) + B \exp \left( -\frac{T_b}{T_s+T} \right) \right]^{-1}
\]

(7)

where \( A \) and \( B \) are constants related to morphology of the network, and \( \sigma(T) \) is the conductivity. The first term is related to quasi-1D metallic conduction, and wherein zone boundary phonons cause backscattering of charge carriers. The energy \( k_B T_m \) is the
backscattering energy of these zone boundary phonons. The second term describes fluctuation-assisted tunneling, which dominates in the low temperature limit. The energy $k_B T_b$ is the energy of the barriers at SWCNT junctions, and the ratio $T_s/T_b$ is determined by quantum tunneling resistivity in the low temperature limit. An idealized example of FAT is shown in Figure 4, where a significant portion of the initial conductivity is retained at low temperatures. Additionally, Figure 4 shows the case of FAT with contributions from phonon scattering (Phonon + FAT), with the effects of phonon scattering only causing a slight decrease in conductivity from the idealized case at higher temperatures. Most of the work to date analyzing SWCNT network transport has been performed on mixed electronic-type networks, because until recently availability of phase pure electronic-type SWCNTs was limited due to lack of good separations techniques. The current knowledge of SWCNT network transport can be broken down into two major categories: SWCNT thin films (translucent) and free-standing SWCNT papers (opaque), with thin films between roughly 10 nm to 300 nm, and free-standing papers (or thick films) greater than 1 µm in thickness.
Figure 4. Idealized forms of different transport models used to analyze SWCNT network conduction. The fluctuation-assisted tunneling model (FAT) shows that a significant fraction of the conductivity is retained at temperatures approaching 0 K. Also shown is the effects of phonon scattering (Phonon + FAT) where phonon scattering causes a decrease in the conductivity at higher temperatures. Two-dimensional variable range hopping transport is also shown (2D-VRH), where the conductivity ~ 0 at temperatures approaching 0 K.

In general, variable range hopping (VRH) conduction models represent the best fit to temperature-dependent resistivity measurements in mixed electronic-type SWCNT films[41, 49, 50]. Some have reported that as the SWCNT network thickness decreases, the conductivity decreases faster with decreasing temperature, which is attributed to increased localization of charge carriers (decrease of $L_{loc}$). For very thin networks, most results find $d = 1$, and as the thickness increases, $d = 2$ or 3. The dimensionality in the
VRH model indicates where the localization is occurring. For instance, \(d = 1\) would indicate that the electrons are localized at the individual SWCNT level, whereas \(d = 2\) or \(3\) would indicated that the localization, and hence, the network resistivity, is controlled more by the junctions[49]. However, these values for \(d\) are sometimes contradicted even within the same research group for nominally identical networks[49, 50], and it is not always clear whether the increased localization occurs at the individual SWCNT level or at SWCNT junctions. Furthermore, when the dimensionality of hopping conduction indicates that the junction resistance is the primary source of resistance in the network \((d = 2\) or \(3)\), it is not known whether the electron localization is strongest within a SWCNT-bundle or at SWCNT-bundle junctions.

In general, has been reported to transition from VRH transport to FAT transport in thicker mixed electronic-type networks (free-standing SWCNT papers)[41, 49, 50]. The primary reason for this description is the analysis of temperature-dependent conductivity (inverse of resistivity), where the conductivity does not become negligible as the temperature approaches zero. This transition was attributed to the M-SWCNTs in the network, as the probability of forming purely M-SWCNT conduction pathways in the network increases with increased thickness. It should be noted that there is some disagreement in the literature, as VRH transport has also been reported for mixed electronic type SWCNT papers. One group reported that the transport followed the VRH model in free-standing SWCNT papers with 65%, and 26% S-SWCNT composition, with changes in the dimensionality from \(d = 2\) to \(d = 3\), respectively[51]. This behavior was attributed to the increase in M-SWCNTs causing a shift to longer localization lengths in the network. It has been proposed that perhaps the resistivity of a mixed electronic-type
SWCNT network can be described by a combination of the VRH and interrupted metallic conduction as[41]

\[
\sigma(T) = \left[A \exp\left(-\frac{T_m}{T}\right) + B \exp\left(-\frac{T_b}{T_b+T}\right)\right]^{-1} + Hexp\left[-\left(\frac{T_b}{T}\right)^\frac{1}{2}\right]
\]

For thinner networks, the 3rd term (VRH) dominates with small contributions from the 2nd term (FAT), and for thicker mixed networks the 2nd term dominates with contributions from 1st term (zone boundary scattering).

Little work has been done in analyzing temperature-dependent resistivity of phase pure or mono-chiral SWCNT thin films. It may be expected that for these more homogeneous networks, the predominantly M-M or S-S junctions will result in lower resistivity due to lower R_J values, and that both would have similar transport properties. Most work comparing transport in M-SWCNT and S-SWCNT thin films has been related to doping effects, with mixed results[47, 52, 53]. A more significant decrease in the sheet resistance was observed for S-SWCNT films as compared to M-SWCNT films upon HNO_3 doping. It was also suggested in all cases that the doping shifts the Fermi level of the S-SWCNTs away from the mid-gap toward the valence band, thus significantly increasing the hole population. This was supported by decreases in absorption, where a high hole population in the valence band leaves few electrons to contribute to absorption. The opinions differed, however, in the transport mechanisms, with changes in the transport being ascribed to R_J between bundles[52], R_J between SWCNTs within the bundles[53], or a combination of R_J and R_CNT[47]. The only temperature-dependent
transport data was presented by Blackburn et al.[52]. They report a transport model of metallic conductivity with a tunneling term

\[ R_S = aT + \beta exp \left( \frac{T_D}{T_s + T} \right) \]  

(9)

where the first term represents metal-like conductivity and the second term is the familiar expression for tunneling between barriers. They claim that both the S-SWCNTs and the M-SWCNTs follow this model, with a much larger decrease in the tunneling term for the S-SWCNT case, indicating that the transport was dominated by barriers at the junction. In contrast, an analysis of free-standing S-SWCNT and M-SWCNT papers found that the S-SWCNT paper exhibited one dimensional VRH transport with strong electron localization, and the M-SWCNT paper exhibited weak localization (i.e. interrupted metallic conduction)[51].

Transport in SWCNT networks is clearly a complex issue, with the intrinsic resistance of SWCNTs and SWCNT-bundles and the resistance at SWCNT junctions each contributing to the overall conduction in the network. The varying sources of resistance create disordered electrical networks, with the network thickness and level of electronic-type enrichment strongly affecting the results. These networks can exhibit weak localization, where metallic transport with thin tunneling barriers is observed, or strong localization, where hopping conduction models such as variable range hopping are a better reflection of the network transport properties. However, there are inconsistencies in the literature in the reported mechanisms and models which describe the transport in these systems. Whether the transport in SWCNT networks follows VRH or interrupted
metallic conduction has not been fully addressed in terms of electronic-type enrichment or network thickness. Although there is general agreement that SWCNT junctions are the primary cause of resistance in the SWCNT networks, there may be evidence that the intra-bundle resistance plays a more dominant role than the inter-bundle resistance. Other open questions are the relative contributions of $R_{\text{CNT}}$ and $R_J$ to the overall network resistance. Thus, there is a need for more systematic studies with phase pure, electronic type-enriched SWCNT networks to identify the appropriate transport models.

### 1.2.2 Electrical Resistance of the CNT-Metal Interface

The other major issue concerning transport in CNT networks is the electrical resistance between CNTs and metal contacts, usually referred to as simply the contact resistance. Consider again Figure 2 and the metal contacts M1 and M2: in a typical scenario metal contacts may enable external electrical connections to the network or between components of the network. Thus, as shown in equation 1, both the resistance of the metals ($R_{M1}, R_{M2}$) and the contact resistance of the CNT-metal interface ($R_{C1}$ and $R_{C2}$) contribute to the overall resistance. Measurement techniques used to attain contact resistance and other important associated values for semiconductor devices have also been applied to CNT-metal interfaces, including single SWCNTs, bulk papers and thin films. The contact resistance between metal and CNTs and the type of contact created (Ohmic vs rectifying) arise from Schottky barriers (SBs) or tunneling barriers at the interface. These barriers can arise from the pure material properties, such as the type of metal, SWCNT electronic type, or diameter, or from external factors such as foreign molecules or oxides introduced by pre- or post-metal deposition processing. Although
there has been extensive research into the nature of transport between CNTs and metals, there are still opportunities for understanding and improving the properties of these systems.

The contact resistance at metal-semiconductor interfaces is traditionally analyzed using assumptions and calculations from the transmission line model. Full derivations from the transmission line model are beyond the scope of the current work, but it results in equations that can be used to measure electrical properties at metal interfaces with other materials. A common technique used to determine the contact resistance is the transfer length method (TLM). Figure 5a shows a typical TLM measurement configuration with metal contacts (yellow) on a planar semiconductor substrate (blue). Using four probes, a constant current is forced through one metal contact to the alternate contact while measuring the voltage drop between the contacts. Measuring the voltage drop across several different lengths gives the total resistance as a function of length. The components that contribute to the potential difference between the contacts are the resistances of the substrate, the metals, and the metal-semiconductor interfaces, which is essentially a re-statement of equation 1. If the two metal contacts are essentially the same, and the resistance of the metals themselves is negligible, then the total resistance from acquired from the voltage measurements is[54]

\[
\frac{\frac{V}{I}}{l} = R_{total} = \frac{R_s}{W} d + 2R_C
\]

where \(R_C\) is the contact resistance and the resistance of the substrate has been re-written in terms of sheet resistance (\(R_s\)). The linear relationship of \(R(d)\) makes acquiring the
contact resistance relatively simple and straightforward. A sample plot of $R$ versus $d$ in Figure 5b illustrates the method, where the “$R$”-intercept is $2R_C$. Additionally the sheet resistance can be acquired from the slope if the width of the contacts ($W$) can be reasonably measured.

Figure 5. (a) Schematic of a common structure with metal contacts on planar substrate used for transfer length method measurements of contact resistance. The metal contacts (yellow) are numbered, with the length ($L$) and width ($W$) of the pads labeled, as well as the substrate length ($d_{ij}$) between contact pads. (b) A TLM plot of measured resistance ($R_{\text{Total}}$) vs $d$, with a linear fit (dashed line) of the data allowing for extraction of the contact resistance ($R_c$), transfer length ($L_T$), and sheet resistance ($R_s$) values.
The contact resistance is useful for statistical process controls or for comparison between similar systems, but the system geometry (contact size, length between contacts, etc.) can change the value of \( R_c \), often making comparisons difficult. For instance, \( R_c \) values of 10 \( \Omega \) and 10 k\( \Omega \) may be possible for the same metal interface if the metal contact geometry is significantly different. A more meaningful value is the specific contact resistance (\( \rho_c \)), measured in \( \Omega \text{ cm}^2 \), which is independent of the contact area, and should ideally be a property of the metal interface of interest. An important term related to the specific contact resistance is the transfer length, which is also shown in Figure 5 as the twice the value of the “d”-intercept. The transfer length is essentially the length over which all of the current is extracted by a metal contact. Common values for many metal-semiconductor transfer lengths are on the order of \( \mu \text{m} \). From these values \( \rho_c \) can be determined either using equation 11 or 12[55],

\[
R_c \approx \frac{\rho_c}{L_TW} \tag{11}
\]

\[
\rho_c \approx R_sL_T^2 \tag{12}
\]

which are accurate approximations for semi-infinite contacts. Contacts are considered semi-infinite when \( L > 1.5 \; L_T \). This simplified transfer length method can be used to acquire values for \( R_c \) and \( R_s \), but values for \( \rho_c \) and \( L_T \) are calculated under the assumption that the sheet resistance of the metal-semiconductor interface (\textit{i.e.}, under the contacts) is the same as the bulk semiconductor sheet resistance. Thus calculations of \( \rho_c \) and \( L_T \) can be erroneous if the sheet resistance under the contact is changed by processing conditions or bonding between the metal and CNTs. Regardless, these values are can be calculated
and are certainly useful for comparison between samples fabricated by identical processing techniques.

All of the methods concerning contact resistance measurements and the transmission line models were developed for metal contacts to planar semiconductors. There are some differences in transitioning from traditional planar substrates to substrates composed of 1D nanostructures, as in the case of metal contacts to single SWCNTs. The resistance of the doped planar substrate becomes the resistance of a single SWCNT (equation 4), and the slope of the R vs contact separation line is now related to the mean free path for charge carriers as opposed to the sheet resistance[37]. Despite these differences the TLM has been implemented for attaining \( R_c \) values for metal contacts to single SWCNTs[37, 56, 57]. For metal contacts to ensemble SWCNT networks, the TLM method is commonly used to find \( R_c \) and \( \rho_c \) with no adjustments to the model. Interestingly, there has been little work analyzing the effects of ensemble nanostructures such as SWCNT thin films on the transmission line model. This may be due to the fact that although a SWCNT film may be poly-disperse in terms of electronic types, sheet resistance measurements are an average of the different individual SWCNT properties and are often consistent across a SWCNT film. The results from the literature for the contact resistance and specific contact resistance values from TLM measurement of metal contacts to CNTs are widely varied. Some of these results are compared and contrasted in Table 1.
Table 1. Values related to TLM measurements for various CNT-metal systems

<table>
<thead>
<tr>
<th>Ref</th>
<th>SWCNT Morphology</th>
<th>Electronic-type</th>
<th>Metal type</th>
<th>R_c (kΩ)</th>
<th>ρ_c (Ωcm²)</th>
<th>L_T (µm)</th>
</tr>
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<td>A[37]</td>
<td>Single-SWCNT</td>
<td>M-SWCNT</td>
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<td>N.S.</td>
<td>N.S.</td>
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<td></td>
<td>S-SWCNT</td>
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<td>3.5×10⁻⁹</td>
<td>N.S.</td>
</tr>
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<td>B[56]</td>
<td>Single-SWCNT</td>
<td>S-SWCNT</td>
<td>Ti/Pd</td>
<td>500</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>C[57]</td>
<td>Single-SWCNT</td>
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<td>Pt</td>
<td>~0.2</td>
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<td>N.S.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr</td>
<td>~4×10⁵</td>
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<td>N.S.</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Cu</td>
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</tr>
<tr>
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<td>Au</td>
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<tr>
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<td>W</td>
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<td>N.S.</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni</td>
<td>~90</td>
<td>N.S.</td>
<td>N.S.</td>
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<tr>
<td>D[58]</td>
<td>Thin film</td>
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<td>Pt</td>
<td>0.575</td>
<td>5.2×10⁴</td>
<td>9.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Cr</td>
<td>N.S.</td>
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<td>55</td>
</tr>
<tr>
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<td></td>
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<td>N.S.</td>
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<td>100</td>
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<tr>
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<td></td>
<td></td>
<td>Au</td>
<td>N.S.</td>
<td>0.05</td>
<td>88</td>
</tr>
<tr>
<td>E[59]</td>
<td>Thin film</td>
<td>Mixed</td>
<td>Ag</td>
<td>N.S.</td>
<td>0.02</td>
<td>80</td>
</tr>
<tr>
<td>F[60]</td>
<td>Thin film</td>
<td>Mixed</td>
<td>Au</td>
<td>N.S.</td>
<td>3.4×10⁻⁵</td>
<td>N.S.</td>
</tr>
<tr>
<td>G[61]</td>
<td>Thin film</td>
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<td>Pt</td>
<td>0.0045</td>
<td>1.1×10⁻⁶</td>
<td>0.38</td>
</tr>
<tr>
<td>H[62]</td>
<td>Thin film</td>
<td>Mixed</td>
<td>Au</td>
<td>~0.5</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
</tbody>
</table>

The data in Table 1 reflects much of what has been seen in reported values. There are few studies in which the specific contact resistance is reported, and studies for TLM values for enriched SWCNT films have been elusive. In the few cases where comparisons for the ρ_c values can be compared, there are significant discrepancies in the reported values. For instance, reference “D” from Table 1 reported a value for ρ_c for Pt that is 2 orders of magnitude higher than observed in reference “G”. The same holds true for Au, where the discrepancy is 3 orders of magnitude (Refs D and F).

A handful of studies have examined the contact resistance after chemical treatment in common SWCNT dopants. There has been some disagreement in the results, as some have claimed enhancement of the CNT-metal interactions while others have claimed the treatments have a negative impact. However, it has been reported that doping with HNO₃
causes a decrease in the contact resistance, but actually increases the specific contact resistance and transfer length values[58, 59]. It was claimed that the chemistry affects the contact, as well as shifting the work function of the S-SWCNTs in such a way as to increase the SB height, although neither mentioned the possibility of an altered sheet resistance beneath the contact, which could affect the accuracy of the reported values.

Some other trends have been reported, claiming that in general, inert metals form the best contacts, followed by carbide-forming metals[57]. They claim the trend is caused by oxygen absorption strongly affects metal-CNT bonds. Also claimed is that metal work functions are somewhat correlated with $R_c$ values, with high work function metals often (but not always) giving better contact to the SWCNTs. There is clearly still a need to characterize these interactions, and determine specific contact resistance values, especially for phase pure SWCNT networks. As mentioned, the values attained for contact resistance and related parameters can be affected by many intrinsic and extrinsic factors. From a fundamental perspective, it is important to understand what these factors are, why they occur, and how they affect the measured values. Thus the discussion in the following section will discuss some of these factors in terms of their contributions to elect

1.3 CNT-Metal Systems and Properties

1.3.1 Schottky Barriers between CNTs and Metals.

Metal-semiconductor interfaces all have contact resistance that arises from transport barriers commonly known as Schottky barriers (SBs). The SB at the metal interface will vary depending on the semiconductor band structure and the metal work function. The
metal work function ($\phi_m$) is the energy required to remove an electron from the Fermi level to vacuum. Similarly, the electron affinity ($\chi$) is the energy difference between the conduction band of a semiconductor and vacuum energy. The SB height is defined as the difference between the metal work function and the electron affinity, as shown in equation 13[54]

$$\phi_B = \phi_M - \chi$$  

At first glance it would seem that the SB is independent of anything but the intrinsic metal and semiconductor properties. However, this is an ideal case, and many other factors can affect the SB height. The Fermi level of the semiconductor will determine the type of contact (Ohmic vs rectifying), and more importantly, interface states or defects may cause Fermi level pinning, which essentially means the Fermi level in the semiconductor is fixed in a mid-gap state, thus making SB-free contact very difficult.

Schottky barriers (SBs) are known to be present for most S-SWCNT and metal contacts and are the primary source of contact resistance, which degrades device performance. Specifically, the SB leads to low current density, rectifying behavior, and inhibits current saturation in single SWCNT and short-channel SWCNT thin film devices. The ability to understand, control, and modify the SBs at SWCNT-metal interface is important because of their impact on device performance.

The SB height for a S-SWCNT/metal junction is commonly defined as the offset between the Fermi level of the metal and a particular band (conduction or valence) of the CNT. This suggests that the metal work function and SWCNT diameter should play
crucial roles in determining the SB height. Since the band-gap ($E_g$) of an S-SWCNT changes with diameter, the Schottky barrier for a particular metal contact to S-SWCNTs should increase as the SWCNT diameter decreases. An illustration of these interactions is shown in Figure 6. Figure 6a shows a representative schematic of the band diagrams for a given metal to SWCNTs of different diameters. The diagram represents S-SWCNTs with small (C), medium (B) and large (A) diameters, clearly showing that in this idealized case, the SB height decreases with increasing SWCNT diameter. The effect of work function on the SB height for Pd (red), Ti(yellow), and Al(green) to the same diameter S-SWCNT is shown in the band diagram in Figure 6b. The high work function of Pd causes its Fermi level to line up almost directly with the valence band of the particular SWCNT (not specified), followed by larger SBs for Ti and Al[63]. Thus the work function of a metal and the SWCNT diameter can be used to predict the offset between a metal’s Fermi level and a particular band of a S-SWCNT for comparison to experimentally determined SBs.
Figure 6. (a) Schematic band diagram depicts the Schottky barrier height differences in three same contacts CNFETs using nanotubes with different diameters. (b) Schematic band diagram depicts the SB differences in three CNFETs with same diameter nanotube, but using Pd, Ti, and Al contacts, respectively. *Reprinted with permission from (Z. H. Chen, et al., "The role of metal-nanotube contact in the performance of carbon nanotube field-effect transistors," Nano Letters, vol. 5, pp. 1497-1502, Jul 2005). Copyright (2005) American Chemical Society[63]. A link to the original article is provided: http://dx.doi.org/10.1021/nl0508624

In semiconductor physics, a common technique for determining the SB height at a metal heterojunction is to perform temperature-dependent $I_d - V_g$ measurements, and extensive research has been conducted to adapt this technique to determine the SBs for various CNT FETs and compare to values predicted by theory. For SB devices the two primary transport mechanisms that affect the measured drain-source current ($I_{ds}$) are tunneling and thermionic emission. From quantum mechanics there is a certain probability of charge carriers to tunnel through a SB, which is strongly dependent on the width of the SB and the presence of an external electric field (i.e., the $V_{ds}$). Thermionic emission current, on the other hand, occurs when the thermal energy of charge carriers exceeds the SB height, and the carriers drift over the boundary either into, or out of the metal. If thermionic emission is the dominant charge transfer mechanism, then the $I_{ds}$
should decrease with temperature at a given $V_{ds}$, an example of which is shown in Figure 7a and Figure 7b[64]. The measured $I_{ds}$ in a FET typically follows an Arrhenius relationship 
\[ I_{ds} \sim e^{-\frac{E_a}{k_B T}} \]
where $E_a$ is the activation energy, $k_B$ is the Boltzman constant, and $T$ is the temperature. Performing temperature-dependent drain voltage sweeps (family of curves) allows the activation energy to be extracted if the log plot of $I_{ds}$ vs $T^{-1}$ is linear, as shown in Figure 7c and Figure 7d[64]. It is not uncommon for researchers to report the calculated activation energy as the actual SB value[65, 66], but this should be done with caution. The activation energy ($E_a$) is the size of the energy barrier at a given temperature and drain-source bias; when determined from $I_d$ as a function of temperature, it is approximately equal to the barrier size of the dominant conduction mechanism under these conditions (i.e., tunneling vs thermionic emission)[66]. For most SWCNT FETs, the dominant charge transfer mechanism at higher temperatures is thermionic emission and will therefore determine the activation energy measured at a particular $V_{ds}$. For instance, in Figure 7c and Figure 7d, at the higher temperatures ($3 \leq 1000/T \leq 8$), thermionic emission dominates, while the lowest two temperatures show a transition to tunneling-dominated charge transfer regime. Thus there will likely be some probability of tunneling even at low $V_{ds}$, hence the true SB is the $E_a$ at zero $V_{ds}$. This can easily be acquired by plotting $E_a$ as a function of $(V_{ds})^{1/2}$ and extrapolating the fit to $V_{ds} = 0V$ and is the common procedure for directly measuring SBs[64, 67, 68].
Figure 7. Temperature dependent (77–285 K) current–voltage characteristics at $V_g = 0$ V of (a) the m-CNT/s-CNT device and (b) the Pd/s-CNT device. The Arrhenius plot of the current at different $V_d$ in the range of 0.1 V to 1 V for (c) the m-CNT/s-CNT device and (d) the Pd/s-CNT device. The bias voltage dependent Schottky barriers are calculated from the slopes of the $\ln I_d$ versus $1000/T$ curves at a higher temperature range for different bias voltages. *Reproduced from Reference [64] with permission of The Royal Society of Chemistry. A link to the original article is provided: http://dx.doi.org/10.1039/c3nr06470k

As has been shown, the presence of SBs can influence the device performance, especially with regard to operating current. Specifically, as the SB height increases, the on-current ($I_{ds}$) decreases logarithmically because of the Arrhenius relation between $I_{ds}$ and the SB. Recall from the discussion of the band diagrams in Figure 6a that the SB
height will decrease as the SWCNT diameter increases. The decrease should be linear with SWCNT diameter because $E_g \propto \frac{1}{d}$. Thus a log-linear increase in $I_{ds}$ is expected as the SWCNT diameter increases. This behavior was observed by Chen et al. and is shown in Figure 8, where $I_{on}$ vs the inverse diameter follows a linear trend, with some deviation for smaller diameter SWCNTs. Using modelling techniques to incorporate the aspects of their specific system, the SBs were estimated from the on- and off-currents. Schottky barriers were determined as ~360 meV for Ti contacts for 1nm diameter SWCNT, and nearly zero SB for Pd contact to a SWCNT with 1.7 nm diameter[63]. This is consistent with what was observed in other work for Pd contacts to S-SWCNTs in which temperature-dependent conductance measurements revealed that for SWCNTs with diameter greater than ~2nm, the contacts were Ohmic and SB-free, and the Pd work function offset to the SWCNT valence band was still relatively low down to 1.7nm ($E_g \sim 0.6$ eV )[2].
A general trend has emerged from research to date, showing that high work function metals have low or even zero SBs to the valence band of larger diameter S-SWCNTs, making them ideal for p-type devices. Conversely, it is expected that low work function metals will create low SBs for n-type conduction, and has been observed in some instances[39, 69, 70], although n-type SWCNT devices have been much more difficult to develop due to the susceptibility of SWCNTs to p-type doping from atmospheric oxygen or chemicals from processing, and that low work function metals are more reactive, readily forming oxides[71]. Though these general trends with metal work function have been observed, experiments to determine the SBs using different devices have shown that the SB height does not scale precisely with the metal work function, and that for smaller diameter SWCNTs (less than ~1.7 nm), the SB is often larger than expected. Deviations from the expected “clean” metal work function trends can be caused by many factors, as
the height and width of the SB can be affected by surface bonding characteristics, the presence of other molecules introduced in processing, and even the gate voltage[68] and gate oxide thickness[66]. It has been observed, for instance, that the presence of oxygen can locally alter the interface potentials, thus altering the expected SB size[57, 72]. In addition to affecting the size of the SBs, some of these extrinsic effects may also create additional tunneling barriers in series with the SBs, making the situation even more complicated. Many of these effects will be discussed in subsequent sections. The divergence from expected trends in diameter can be seen in Figure 8 as the $I_{ds}$ values deviate from linearity at smaller diameters. These effects have not been fully explained but are sometimes attributed to the reactivity of smaller diameter SWCNTs with certain metals.

Although much work has been done to understand and measure the SBs of various metals to CNTs, there is still a wide variation in reported values and observed trends, indicating that the current knowledge is incomplete. According to one review of the subject, “as is evident from the large discrepancies in both theoretical and experimental results, there is still a lack of understanding of the details of the SB formation and the influence of interface dipoles”[24]. There is also still opportunity to improve the contacts for metals to SWCNTs, as the performance of many short-channel thin film devices and single SWCNT devices is still hampered by the presence of SBs. This is especially true for small diameter SWCNTs, where making good metal contacts becomes more difficult due to larger band-gaps and structure-influenced bonding characteristics.
1.3.2 CNT-Metal Bonding Interactions

Bonding between metals and CNTs can also have significant impact on the mechanical and electrical performance of CNT-metal interfaces and the resulting metal morphology. In addition to affecting the adhesion and mechanical integrity of the CNT-metal interface, bonding interactions between CNTs and metals can alter the SB size, and contribute additional tunneling barriers. It has been shown in simulations that the change in the equilibrium bonding distance between a particular metal and CNT resulting from different crystal orientations produces different SB and tunneling barrier heights. The resulting values are shown in Table 2 for Au, Pd, and Pt. Additionally, a tunnel barrier height of almost 2 eV was found for Au (111) at equilibrium. These differences may contribute to the variation in values reported for a particular metal contact to CNTs even when the experimental conditions are nearly identical[73]. Hence the bonding and wettability of metals to CNTs is an important subject regarding the physical and electrical properties of CNT-metal interfaces and depends on the type of metal and deposition method[23]. Good wetting of a given metal onto CNTs also provides more injection points for carriers, and generally promotes Ohmic contact to the CNTs. In addition to affecting the electrical performance, metals that effectively wet CNTs will ensure more mechanically stable contacts, which is especially important for CNT flexible electronic applications and metal matrix composites.
Initial investigations with metal on CVD-grown suspended SWCNTs showed that the wettability followed the trend Ti>Ni>Pd>Fe>Al>Au, as depicted in Figure 9. Smaller, more uniform particles are seen evenly distributed along the CNT for Ti, Ni and Pd, while the Au, Al, and Fe particles are larger and more variable in size. The trend in wettability was suggested to be related to the binding energy between each metal and SWCNT[74]. It is generally agreed that this trend is correlated to the number of vacancies in the d-orbital[74, 75]; however this relationship is not fully consistent with all metals and CNTs as there are other variables that can affect wetting interaction, such as CNT band structure, form factor, and the presence of intermediate molecules. For instance, the diameter of a SWCNT, whether semiconducting or metallic, also affects the surface energy, as smaller SWCNTs tend to be more reactive and more prone to defects. The variance in surface energy with diameter will affect the surface bond quality and change the wettability of the CNTs with different metals, which can give rise to additional carrier injection barriers[23, 63]. As an example, it was shown that Pd makes reliable Ohmic contact to metallic SWCNTs if the diameter is sufficiently large (i.e., >1.5nm)[3] and later members of the same group reported similar results with Rh. However, for smaller diameters non-linear I-V characteristics near zero volts indicated
non-Ohmic contact and the conductance dropped significantly as the SWCNT diameter approached 1.2nm[23]. This was attributed to a tunnel barrier at the CNT-metal interface caused by the reactivity of the small diameter SWCNTs because for metallic CNTs, there should be no band-gap, and hence no SB. However, it is possible for some zigzag metallic SWCNTs to have small band-gaps (≤100 meV), and for metallic bundles to have pseudo band-gaps[76], so the nonlinear I-V characteristics could also be due to very small SBs at the metal interface.

Figure 9. TEM images of: (a) Ti, (b) Ni, (c) Pd, (d) Au, (e) Al, (f) Fe coating on carbon nanotubes with a thickness of 15 nm. *Reprinted from Chemical Physics Letters, vol. 331, Y. Zhang, et al., "Metal coating on suspended carbon nanotubes and its implication to metal–tube interaction," pp. 35-41, Copyright (2000), with permission from Elsevier[74]. A link to the article is provided: http://dx.doi.org/10.1016/S0009-2614(00)01162-3

The effects of wettability of metal to CNTs on the electrical performance of devices have been demonstrated experimentally. For instance, the performance of Li-ion batteries with SWCNT anodes coated with Ti and Ni were compared. SEM images of the Ni-
SWCNT and Ti-SWCNT interface revealed more conformal coating of the Ti, thus indicating better wetting of the CNT surface than Ni, which is consistent with other work[77]. The result was a significant improvement in battery performance using the Ti-coated anode, partially attributed to the better wetting of the Ti to the SWCNTs. It has also been shown for various metal contacts to mixed electronic-type SWCNT networks that the contact resistance is strongly correlated to the wettability, and that the better the wettability, the lower the contact resistance[75].

There is clear evidence that attaining better wetting and more conformal metal coatings should, in most cases, lead to an improvement in electrical properties of the CNT-metal interfaces and consequently in device performance. Thus, various surface treatments have been developed for improving the wetting of various metals to CNTs and will be discussed in the following section.

1.3.3 Chemical/Physical Modifications of CNT-Metal Systems

There are a number of physical and chemical factors besides the intrinsic properties of CNTs and metals that may affect these interfaces, which are a result of modifying the CNTs or the CNT-metal system. “Modifications” is a broad term, but generally relates to alteration of electrical, vibrational or surface energies of the SWCNTs or metals. These modifications can be intentional or unintentional, and developing an understanding of how to either avoid or implement the modifications during device processing is imperative for developing better CNT-metal interfaces.

Unintentional modifications could include processing steps in which foreign molecules or bond alterations are introduced into the CNT-metal interface, inevitably
changing the properties of the system. Adsorbates from the atmosphere, doping agents, and residual surfactant molecules from solution-based processing are some of the possible sources of this unintentional modification. These foreign molecules essentially form a layer between the CNTs and the metal, which may enhance or degrade the electrical and bonding interactions. One example mentioned in the discussion of contact resistance is chemical doping, which has been observed to decrease the sheet resistance of SWCNTs, but the effect on the metal interface is difficult to discern. It was suggested that the doping shifts the Fermi level of the SWCNTs in a way that enhances the electrical interactions with the metal. If this is the case then doping would not enhance all metal contacts, as it may shift the Fermi level of the SWCNTs away from the Fermi level of the metal. There are numerous other processing variables that could be assessed in a similar manner, which should ultimately inform the fabrication processes when the electrical interactions of the CNTs and metals are of concern.

It is common to intentionally modify the CNT-metal interface to enhance its material properties. Examples of intentional modifications include chemical and physical functionalization techniques, various thermal treatments, or introduction of intermediate materials between the metal and CNTs. As an example, indirect evidence of enhanced contact resistance was observed by joule heating of a MWCNT and W tip in contact. High currents caused fusion and W-carbide formation, which greatly reduced the overall resistance from 10.2 to 0.7 kΩ when the ends were fused[78]. This is just one example of many, as there are nearly endless ways to modify CNT-metal networks pre- and post-metal deposition.
1.4 Carbon Nanotubes for Space Applications

Many of the CNT-based devices discussed thus far are attractive for space applications because of the electrical and mechanical properties of the CNTs, as well as potential weight savings and radiation stability[4, 5]. In fact, CNTs have already been utilized for space exploration in NASA’s JUNO mission, an orbiter sent to explore Jupiter’s strong magnetic field and magnetosphere. The CNTs were utilized in a multifunctional composite, providing structural reinforcement and electrostatic dissipation, grounding, and electromagnetic shielding[79]. The CNTs used in this mission will be exposed to a number of environmental conditions, including radiation belts thousands of times stronger than Earth’s Van Allen belts[80]. Harsh radiation environments are a general concern for all space exploration, motivating the need to understand the response of CNTs to various types of radiation, including ion irradiation.

It is known that ions or electrons of sufficient energy and dose can create displacement damage effects in SWCNTs, which refers to displacement of C atoms (i.e., vacancy formation) from the structure[81-83]. High doses of ion irradiation produce vacancies and other defects by primary and secondary ion collisions[84, 85], causing degradation of CNT structural and electronic properties[82, 86-88]. Raman spectroscopy and electrical transport are common techniques for characterizing irradiation damage, especially for ensemble structures like thin films or bulk papers. Raman analysis of ion-irradiated single-wall carbon nanotubes (SWCNTs) reveals increasing D/G and D/G’ ratios, and relative decreases in the radial breathing modes (RBMs) as ion fluence increases[83, 89, 90], all of which indicate the presence of increasing defect concentration. At very high fluences, depending on the ion species and energy, the G’ and RBM bands are completely
suppressed and peak broadening of the D and G bands are observed[83, 91], indicating significant defect generation in the SWCNTs. In the case of electrical transport measurements, a monotonic increase in the sheet resistance has been observed with increasing ion fluence[41, 50, 81, 83, 92]. It has also been found that the relative increase in sheet resistance and the relative increase in D/G' ratios from Raman analysis are nearly identical for a given displacement damage dose. In fact, regardless of the electronic type or incident ion species, the opto-electronic response to displacement damage follows a very consistent trend, which even extends to other nanostructured carbons like graphene[83]. There are also other considerations for space exploration, including environmental aspects like high vacuum, extreme temperatures and thermal shock, as well as mechanical and vibrational stresses experienced from launch conditions, mounting, etc. The response of CNTs themselves has been investigated for a number of these issues; however, limited work has been done to explore CNT-metal interactions and for space environments. In particular, this dissertation focuses on ion irradiation and development of more mechanically robust CNT-metal structures.
2 Dissertation Overview

The goal of this work is to fabricate test structures composed of metal contacts to CNT networks and to characterize the CNT-metal interfaces using microscopy, electrical, and mechanical measurements to develop a fundamental understanding of their material properties as a function of metal composition and CNT morphology and structural properties. Changes in the electrical and mechanical properties will be further evaluated in response to chemical and structural modifications. Understanding changes in the physical and electrical properties of different CNT-metal interfaces in response to chemical or physical modifications will enable determination of appropriate processing conditions for fabricating optimized metal contacts to SWCNT networks. Exploration of the response of CNT-metal interfaces to extreme environmental conditions would benefit space technologies which seek to implement SWCNT devices, because of the extreme temperature fluctuations, mechanical/vibrational shock, and harsh radiation environments that can exist in space.

The dissertation is organized according to three primary research focus areas, based on the topics and funded research projects undertaken during the course of this work. The following list (numbered) outlines the primary research focus areas:

1. Electrochemical defect tagging with metal nanoparticles
2. Ion irradiation effects on the CNT-metal interface
3. CNT metal matrix composite electrodes

Chapter 3 discusses standard procedures used in synthesis, purification, and fabrication of various CNT networks. Chapter 4 describes research into whether
SWCNT-metal electrochemical interactions can be exploited for spatial mapping of ion-irradiation induced defects. Chapter 5 utilizes Ag contacts to SWCNT thin films, and investigates how ion irradiation-induced defects change the electrical properties of the SWCNT-Ag interface. Finally, Chapter 6 explores whether CNTs can be utilized as a reinforcement material in layered metal matrix composite (MMC) electrodes. The MMC work addresses appropriate fabrication techniques, and the impact of CNTs on metal grain structure, mechanical properties, and electrical performance of CNT-MMCS to mechanical stress. Each of these topics and the necessity of the work will be further motivated at the beginning of its respective chapter.
3 Standard Experimental Procedures

3.1 CNT Synthesis and Purification

Methods for synthesizing, purifying, and separating SWCNTs can vary, as discussed in section 1.1, producing SWCNTs with different diameters, electronic types, and defect content. SWCNTs used in all experiments described in this dissertation were synthesized and purified in-house in the NanoPower Research Labs (NPRL) using established procedures[11, 28], unless explicitly stated otherwise. The SWCNT synthesis is performed by laser vaporization techniques using Ar carrier gas at 1150 °C with an Nd:YAG (1064 nm) laser, which vaporizes a nano-metal catalyst (3 wt% Ni and 3 wt% Co)-graphite target. The raw soot produced by the laser vaporization is purified by a 16 hour acid reflux with 300 mg soot, 300 mL DI H₂O, 30 mL of HCl (37%), and 72 mL of HNO₃ (70%), which removes some of the catalyst particles. The reflux solution is filtered into paper form using vacuum filtration onto polytetrafluoroethylene (PTFE) filter paper. The resulting SWCNT paper is thermally oxidized with a ramp-stop at 10 °C/minute to 560°C to remove any amorphous carbon impurities. This additionally “cracks” carbon encasing un-reacted catalyst particles. The SWCNT paper is then further purified by a concentrated HCl soak for 1 hour to remove any residual Ni/Co catalyst particles and a final thermal oxidation step.
3.2 CNT Network Fabrication Techniques

A majority of the SWCNT networks employed in these studies were fabricated as either free-standing papers or thin films. CNT thin films may be deposited on glass, metal thin films, or more traditional semiconductor substrates such as SiO$_2$, GaAs, or InP.

3.2.1 Free-standing CNT Paper Fabrication

Free standing CNT papers were fabricated by vacuum filtration of SWCNTs dispersed in either organic solvents (e.g. DMA) or surfactants onto filter membranes. All surfactant dispersions used in this work utilized sodium dodecyl-sulfate (SDS) as a dispersing agent, but the techniques are equally adaptable to other known CNT dispersants such as sodium deoxycholate (DOC). The filter membranes used to fabricate free-standing CNT papers in the present work were composed of polytetrafluoroethylene (PTFE). After filtering the CNT dispersion onto the PTFE membrane, the films are rinsed with water, followed by acetone rinsing (for drying). The CNT papers are released from the filter membrane by applying tensile stress to the membrane at several points on opposing sides, or essentially stretching the membrane with gloved hands to the point the CNT paper simply releases from the membrane. The final paper can be easily handled with tweezers and cut into desired shapes for various experiments.

3.2.2 CNT Thin Film Fabrication

The primary technique for fabricating CNT thin films was the MCE-transfer method, in which SWCNTs are dispersed by ultra-sonication into surfactants such as sodium dodecyl sulfate (SDS) or sodium deoxycholate (DOC) and vacuum filtered onto mixed
cellulose ester (MCE) papers, thus creating a SWCNT thin film. The thickness of the film can be controlled by adjusting the volume of dispersion used during vacuum filtration, and is typically characterized by a mass density based on the concentration, volume and size of the filter membrane (i.e. µg/cm²). Once the SWCNT film has been fabricated, it can be transferred to a variety of substrates, such as glass, quartz, or semiconductor wafers. The film deposition is achieved by mechanical transfer to the substrate after soaking in ethanol. Once pressed onto the appropriate substrate, the film/substrate is immediately placed in an acetone bath, which begins dissolving the MCE membrane. After several successive acetone baths (30 minutes each), the SWCNT film remains adhered to the substrate, which is washed with acetone, isopropyl alcohol, and copious amounts of water, and dried. The film is then typically exposed to a mild thermal oxidation “cleaning” step at 300 °C for 2 hours in air to remove any residual MCE, surfactant, or solvents. Another thin film fabrication technique is to deposit thin films from chlorosulfonic acid (CSA). By this technique, SWCNTs are dispersed in CSA and vacuum filtered onto alumina (Al₂O₃) membranes and subsequently transferred to the substrate of choice. By placing the SWCNTs in contact with a substrate and rinsing the alumina filter with water from the reverse side, the SWCNT film releases, adhering to the substrate. The CSA films can also be transferred by immersing the alumina filter in water, causing the SWCNT film to float off of the filter. A “scooping” technique is used to retrieve the film using the desired substrate. Other methods for SWCNT film fabrication may be pursued if necessary, including drop casting and ultrasonic spray techniques.
4 Spatial Defect Profiling


4.1 Introduction

The intrinsic changes in SWCNT structure in response to ion irradiation as discussed in Chapter 1.4 are fairly well understood; however, there is added desire for high resolution profiling of the resulting defects in CNTs. Spatial profiling to quantify the location and defect density in different CNT networks based upon varying radiation conditions (e.g., source, fluence, angle of incidence, etc.) is a combination of detecting the presence of defects and achieving nanometer-level resolution. Studies to date have focused on Raman mapping and microscopy, but there are limitations in terms of experimental timescale to achieve nanometer resolution and large sample area for analysis. In the case of far-field Raman, resolution is diffraction limited to $\lambda/2$ (e.g., 316.5 nm resolution for 633 nm laser) for normal mapping capabilities[94, 95], whereas near-field Raman techniques can achieve significantly better resolution (10 nm – 30 nm)[29] but are typically useful for locating defects in single CNTs, rendering the technique ineffective for assessment of large area samples or nanotube ensembles.
Methods such as transmission electron microscopy (TEM)[96], scanning transmission microscopy (STM)[97, 98], and scanning gate microscopy (SGM)[99, 100] are capable of resolving individual defects, but the time and sample preparation required are not practical for acquiring statistically significant defect distributions, especially in ensemble networks of CNTs such as thin films or bulk papers. Thus, the proper combination of spectroscopy with microscopy could be established to achieve nanometer resolution and large area spatial mapping if a visual indicator is developed to “tag” the location of defects.

One promising method to identify the presence of defects on irradiation-damaged SWCNTs is through a selective metal nanoparticle (NP) deposition. Recent work has shown that a number of metals will nucleate at CNT defect sites through various electrochemical[30, 101], spontaneous reduction[102, 103], and chemical functionalization techniques[104, 105]. Electrochemical techniques require electrochemical cell fabrication and very specific overpotentials to achieve controllable NP deposition. Spontaneous reduction or electroless deposition of Ag, Au, and Ni on individual SWCNTs and ensemble networks has been demonstrated, but statistical analysis of controlled nucleation for particle size and distribution has been limited. Studies to investigate metal NP nucleation onto ion irradiation-induced defects in SWCNTs have been elusive, and such a process may also be of interest to applications in which specific particle size and density are needed (i.e., catalysis and sensing). Ultimately, the prospect of using selective metal deposition in conjunction with scanning electron microscopy (SEM) to observe large numbers of NPs nucleated onto defect sites can provide an approach for spatial defect profiling.
In this work, a rapid solution-based method for selective deposition of Au-NPs onto ion-irradiated SWCNT papers has been developed, along with SEM characterization to attain particle nucleation statistics. SWCNT papers irradiated with 150 keV $^{11}$B$^+$ and exposed to 0.01M KAuBr$_4$(aq) were observed via SEM and the distribution of nucleated Au-NPs were characterized as a function of irradiation dose and KAuBr$_4$(aq)-exposure time using particle counting image analysis techniques. Raman spectroscopy was used to measure the response from structural damage due to ion irradiation and resulting interactions from the Au-NP nucleation process. This study, supported by statistical analysis, summarizes a technique that can be extended to other radiation environments to monitor defect generation, while also providing information about the fundamental interactions between Au-NPs and SWCNTs.

4.2 Experimental Methods

SWCNTs were synthesized in-house via laser vaporization, purified, and fabricated as free-standing papers. The standard HCl and thermal oxidation purification (chapter 3.1) was performed twice, re-dispersing SWCNTs in dimethylacetamide (DMA) between each step to produce very high purity SWCNT papers. The purity of the sample was verified qualitatively via SEM using a Hitachi S900 field emission instrument at 2kV accelerating voltage, and quantitatively via optical absorption spectroscopy using a Perkin Elmer Lambda 900 Spectrometer.

Purified SWCNT papers were controllably irradiated in vacuo ($<5\times10^{-6}$ Torr) with 150 keV $^{11}$B$^+$ to specific fluences between $1\times10^{13}$ ($^{11}$B$^+$)/cm$^2$ to $1\times10^{15}$ ($^{11}$B$^+$)/cm$^2$ using a medium current Varian 350-D ion implanter. The ion beam was rastered uniformly over
196 cm$^2$ (triangular waveform, X-raster: 1019 Hz, Y-raster: 117 Hz, 20 Vpp) with beam currents ranging from 9 µA at the lowest fluence (30 second implant) to 90 µA at the highest fluence (5.5 minute implant). The sample temperature was maintained at approximately 25°C by water cooling of the copper chuck. Purified and irradiated SWCNT papers were immersed for a fixed time (ranging from 30 seconds to 10 minutes) in 0.01M aqueous solutions of KAuBr$_4$ (Sigma Aldrich), prepared directly prior to each experiment. After immersion in 0.01M KAuBr$_4$(aq), the samples were immediately rinsed with DI H$_2$O to quench any Au nucleation, followed by drying in a vacuum oven at 100°C and pressure of ~100 mTorr for 2 hours.

Both purified and irradiated SWCNT papers were analyzed before and after KAuBr$_4$ exposure and compared via Raman spectroscopy. Linear background subtraction was performed on each SWCNT spectrum. The SWCNT morphology and Au nucleation were investigated via SEM.

Au-NP nucleation statistics were obtained using the ImageJ software package. The SEM images (50,000× magnification) were calibrated using measuring tools in ImageJ to set the global scale for all images to that of the scale given by the SEM. The threshold function was used to saturate pixels for the Au-NPs to determine particle locations. The particle analyzer tool was used to output masks of saturated pixels and the output masks were subsequently merged into one final mask for analysis. The number and area distribution of visible Au-NPs in the final mask were output by the particle analyzer tool.
4.3 Results and Analysis

The SWCNT paper purity is a critical property in eliminating ambiguity from interpreting residual metal catalysts as Au-NPs from electrochemical deposition. Laser produced SWCNTs inherently have a low defect content[106], and additional steps were taken to remove “all” catalyst particles during purification. Thus, UV-visible absorption spectra and SEM were rigorously used to assess the effectiveness of the purification techniques of the starting material. The purity of the SWCNT bulk paper in terms of amorphous carbon content was determined to be equivalent to the 100% pure reference sample based on the ratio of the absorption intensity (see Figure 10a) of the semiconducting ($S_{E22}$) and metallic ($M_{E11}$) peaks[11]. SEM analysis (see Figure 10b) confirmed that the HCl purification procedure effectively removed the catalyst particles.

Figure 10. (a) The UV-visible absorption spectrum of the purified SWCNT papers with the prominent metallic ($M_{E11}$) and semiconducting ($S_{E22}$) peaks labeled. (b) SEM image at 50,000× magnification of the high purity SWCNT paper.
Particle nucleation studies were conducted to understand the selectivity of using a 0.01M KAuBr\textsubscript{4(aq)} solution to nucleate Au-NPs on defective SWCNTs. Initially, a purified SWCNT paper (represented by the SEM shown in Figure 10b) was partially masked by quartz and irradiated with \(1 \times 10^{15} (^{11}\text{B}^+) / \text{cm}^2\). The mean penetration depth of 150 keV \(^{11}\text{B}^+\) in quartz is ~500 nm, as approximated by SRIM\textsuperscript{[107]} calculations, confirming that the 650 ± 3 µm quartz mask was sufficient to terminate all ions. In the exposed regions, the prominent Raman modes are significantly affected by the irradiation, including broadening of the D and G bands and nearly a complete suppression of the G' band (see Figure A.1a), which is consistent with previous work\textsuperscript{[83]}. This high dose helps to ensure that there are enough defects sites to make the Au-NP-tagged region obvious in subsequent SEM analysis. Figure 11 shows SEM images at (a) 10,000× and (b) 30,000× magnification of the irradiated/masked SWCNT paper after immersion in 0.01M KAuBr\textsubscript{4(aq)} for 1 minute. The images clearly illustrate the boundary between the irradiated (left) and quartz-masked (right) sides. Control experiments with purified SWCNT papers exposed to 0.01 M KAuBr\textsubscript{4(aq)} for 30 seconds, 3 minutes, and 10 minutes showed only sparse nucleation (see Figure A.2 SEM images). These results are similar to what is observed on the quartz-masked portions of the images in Figure 11. It is important to note that Au-NP nucleation may be observed in purified SWCNTs as a result of initial SWCNT defect concentration caused by synthesis and purification techniques or spontaneous reduction of the precursor\textsuperscript{[108, 109]}. However, the selectivity of Au nucleation onto ion-irradiated SWCNTs (and not onto purified SWCNTs) shows that the technique can be used to investigate spatial distributions of ion irradiation-induced defects as well as potentially being used to controllably deposit Au-NPs onto SWCNTs.
for other applications. These results support the ongoing interest to identify the location and spatial distribution of defects in SWCNT materials, and presently are shown for an ensemble network of irradiated SWCNTs.

![SEM images of purified SWCNT paper with quartz mask](image)

Figure 11. SEM images at (a) 10,000× magnification and (b) 30,000× magnification of a purified SWCNT paper which was partially masked by quartz (650 µm thickness) during ion irradiation at 1×10¹⁵ (11B⁺)/cm² and subsequently exposed to 0.01M KAuBr₄(aq) for 1 minute. The dashed line demarcates the boundary of the quartz mask which highlights the Au-NP nucleation on the irradiated SWCNTs compared to the quartz-masked region.

The Au-NP nucleation process was investigated as a function of KAuBr₄(aq)-exposure time at a constant fluence to determine a suitable method for spatial profiling of defective SWCNTs. The intent is to identify exposure conditions which rapidly saturate all available nucleation sites with Au-NPs while minimizing particle size from Ostwald ripening[110]. The SWCNT papers were irradiated at 5×10¹⁴ (¹¹B⁺)/cm² to retain more SWCNT structural character compared to 1×10¹⁵ (¹¹B⁺)/cm². The D/G and D/G′ ratios of the Raman spectra support this assertion (see Figures S1c and S1d), however, substantial
damage to the SWCNTs is confirmed. In contrast, the pre- and post-irradiated SWCNT SEM micrographs in Figure 10b and Figure 12a, respectively, reveal no significant visual changes induced by ion irradiation. The prominent nanotube morphology still exists and no carbonaceous impurities are apparent. Subsequent to irradiation, separate samples were immersed in 0.01M KAuBr₄(aq) for 30 seconds, 3 minutes, or 10 minutes and SEM images for each sample are shown in Figure 12b-d, respectively. The nucleation of Au-NPs is observed at all exposure times confirming the efficacy of Au-NP deposition onto defective SWCNTs. Qualitatively, the size of the Au-NPs for the 30 second exposure (see Figure 12b) appears to be smaller than the particles in the 3 minute and 10 minute exposures (see Figure 12c and 3d, respectively), yet the total density (i.e., Au-NPs/µm²) remains nearly constant for all three exposure times. Quantitative analysis of the particle distributions, based on Au-NP radii and density, is provided below.

The calculated Au-NP radius for each exposure time was quantified by using the particle area measurements given by image analysis of five representative images and assuming a circular geometry. Histograms of the Au-NP radii are shown in Figure 13a-c for each exposure condition, respectively. In general, the distributions are weighted toward smaller NPs for 30 second KAuBr₄(aq) exposure (Figure 12b), as compared to 3 minute or 10 minute exposure times. The mean Au-NP radii for 30 second, 3 minute and 10 minute KAuBr₄(aq) exposures were calculated as 15 ± 4, 19 ± 6, and 21± 6 nm, respectively. Similarly, the median radii for 30 second, 3 minute and 10 minute KAuBr₄(aq) exposures were calculated to equal 14, 18, and 21 nm, respectively. In some applications, such as chemical sensing and catalysis, a uniform particle size is critical[101, 111, 112], and Figure 13d compares the cumulative distribution for these
samples. The 30 second sample exhibits the largest slope (as indicated by the weight average trend line) at the inflection point compared to the other KAuBr$_4$(aq) exposure times. The short exposure time represents a rapid, controlled nucleation and growth, with a narrow distribution of Au-NP sizes. Overall, the timescale for Au-NP nucleation (~30 seconds) and growth (>3min) in the bundled SWCNT networks is consistent with work on single SWCNTs grown on SiO$_2$[109], where the average particle radius increases with longer exposure time due to particle coalescence as growth occurs. In addition, particle counting is necessary to determine the time sufficient for Au-NP nucleation at all available sites. Thus, the visible Au-NP count was measured as part of the image analysis. The particle density for 30 second, 3 minute and 10 minute KAuBr$_4$(aq) exposures were 16, 17 and 13 Au-NPs/µm$^2$, respectively. The slight decrease in density for the longest exposure time may be a result of Au-NP coalescence. As a point of comparison, the purified SWCNT papers exhibit an intrinsic particle density of residual Ni/Co catalyst particle <<1/µm$^2$. Therefore, the collective results show that Au-NP size increases with exposure time, however, 30 seconds is sufficient time to yield a saturated density of Au-NPs since the particle density remains relatively constant for longer times.
Figure 12. SEM images at 50,000× magnification for the (a) purified SWCNT paper irradiated to a fluence of $5\times 10^{14} \text{(11B+)}/\text{cm}^2$ and exposed to 0.01M KAuBr$_4$(aq) for (b) 30 seconds, (c) 3 minutes, and (d) 10 minutes.
Figure 13. Histograms of Au-NP radii for purified SWCNT papers irradiated with $5 \times 10^{14}$ (11B$^+$)/cm$^2$ and exposed to 0.01M KAuBr$_4$(aq) for (a) 30sec, (b) 3 min, and (c) 10min. (d) The corresponding cumulative distribution plots are overlaid and the dashed lines represent a weighted trend line through each data set for visual clarity.

SWCNT papers were exposed to different 150 keV $^{11}$B$^+$ fluences to modify the number of defects and determine if a corresponding change in the number of nucleation sites is observed. Representative portions of a purified SWCNT paper were irradiated at fluences of $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$, and $1 \times 10^{15}$ (11B$^+$)/cm$^2$ and exposed to 0.01M
KAuBr₄(aq) for 30 seconds. SEM micrographs for each irradiated SWCNT sample after KAuBr₄(aq) exposure are shown in Figure 14. A clear trend emerges, whereby an increase in Au-NP density is observed with increasing fluence. Ten representative images for each exposure time were selected for statistical image analysis. The cumulative distributions (see Figure A.3) consistently show that all fluences with 30 second exposure produce similar Au-NP radii, suggesting that the samples were irradiated uniformly, producing similar types of defects that initiate nucleation. The particle density increases from 3 Au-NPs/µm² at a fluence of 1×10¹³ (^{11}B⁺)/cm² to 58 Au-NPs/µm² at a fluence of 1×10¹⁵ (^{11}B⁺)/cm². In addition, the center-to-center distances between Au-NPs residing along the same SWCNT bundle were measured for the SEM images in Figure 14 and are summarized in Figure A.4. The mean inter-particle distance decreased from 216 nm for 1×10¹⁴ (^{11}B⁺)/cm² to 74 nm for 1×10¹⁵ (^{11}B⁺)/cm², based on image analysis of the data shown in Figure A.4. The particle spacing data is provided for all fluences except 1×10¹³ (^{11}B⁺)/cm², because there were not a statistically significant number of Au-NPs clearly residing along the same bundle in the images. This decrease in inter-particle distance is consistent with the uniform distribution of defects at higher fluence that is supported by an inter-vacancy length model[83]. The SEM analysis of the particles thus affirms that the Au-NP tagging technique is sensitive enough to distinguish between different radiation doses.
Figure 14. SEM images at 50,000× magnification for the SWCNT papers exposed to 0.01 M KAuB4(aq) for 30 seconds after 150 keV 11B+ irradiation at fluences of (a) $1 \times 10^{13}$ ($(11B^+)$)/cm², (b) $1 \times 10^{14}$ ($(11B^+)$)/cm², (c) $5 \times 10^{14}$ ($(11B^+)$)/cm², and (d) $1 \times 10^{15}$ ($(11B^+)$)/cm².

The observed increase in Au-NP density is expected to correlate with higher intrinsic structural damage to the SWCNTs, however, comparison with Raman can provide a direct probe of ion-generated defects for SWCNTs and validate this model. When the
purified SWCNTs are irradiated at increasing $^{11}$B$^+$ fluence, the D band intensity increases, while the G and G' band intensities decrease (see Figure A.1a). At higher fluences (i.e., $1 \times 10^{15}$ ($^{11}$B$^+$)/cm$^2$), peak broadening is observed and the G' band is barely distinguished above the noise floor. The degradation of the Raman spectra for the purified laser-synthesized SWCNT papers is consistent with reported values for irradiated electronic-type-separated arc SWCNT thin-films. Figure 15a shows the relative change in the D/G' ratio (i.e., normalized to the initial D/G' ratio of the starting material) for each irradiated SWCNT paper prior to Au-NP nucleation. The measured Au-NP density after exposure to KAuBr$_4$(aq) (as quantified by the image processing of data from Figure 14) is overlaid with the relative changes in the D/G' peak ratios. A relative increase in the D/G' ratio (□) with increasing fluence is observed and tracks directly with the particle density (◊). These results clearly show a strong correlation between the structural degradation of the SWCNTs (as measured via D/G') and the Au-NP density (measured via image analysis). Since the D/G' ratio corresponds to an increase in the number of defects and there is a concomitant increase in particle density, the direct correlation implies that the Au-NP deposition is tagging a consistent fraction of additional defects at increasing fluence. This result is exemplified by the particle density plotted as a function of relative change in D/G' ratio values (see Figure 15a inset). The dashed line represents a linear fit ($R^2 = 0.998$) to the data, and the equation of the line can be used as a calibration for the Au-NP density that could be achieved if desired. Overall, the approach directly shows a method to assess different levels of radiation exposure (i.e., dosimetry) as well as the ability to tune the number of Au-NPs on the surface by varying radiation conditions.
Figure 15. (a) The relative change in D/G' peak ratio values (□) and the Au-NP density (◊) are plotted versus fluence. The inset shows the particle density plotted versus the relative change in D/G' ratios, with the dashed line representing a linear fit (R² = 0.998) to the data and the equation of the line shown. (b) The G'-band peak positions from 633 nm laser excitation for irradiated SWCNTs before (□) and after (◊) KAuBr₄(aq) exposure are plotted versus fluence.

Additional analysis of the Raman spectra for irradiated SWCNT papers and after exposure to KAuBr₄(aq) can provide fundamental understanding of the material changes from the irradiation process as well as the Au-deposition onto SWCNTs (see Figure A.1). Consistent shifts are observed for each of the various peaks at increasing fluence, with the most prominent being for the G'-band. Figure 15b illustrates the maximum peak positions from Lorentzian-fitted line-shapes for the G'-band as a function of fluence up to 5×10¹⁴ (¹¹B⁺)/cm², beyond which the peak is suppressed. The peaks systematically shift toward lower wavenumber with increasing fluence, with a shift of 11 cm⁻¹ at 5×10¹⁴ (¹¹B⁺)/cm² for irradiated-only SWCNTs (□). This behavior may relate to a blue-shift in absorption energy from the irradiated SWCNTs [83], but could also signify charge-induced renormalization of the electronic and vibrational energies of the SWCNTs.
attributed to doping[29]. Raman spectra of purified SWCNTs exposed to KAuBr\textsubscript{4}(aq) (see Figure A.1b), exhibit a quenching of the BWF-lineshape similar to other studies[108]. In addition, there is G'-band quenching relative to the G-band, and shifts in the G'-band peak position (◊) as high as 13 cm\textsuperscript{-1} (see Figure 15b), attributed to charge transfer between the ionic species and the SWCNTs[19]. The D/G and D/G' ratios were analyzed as a function of fluence (see Figure A.1c and d, respectively) for the SWCNTs before (□) and after (◊) Au-NP nucleation. At lower fluence, a decrease in the D/G ratios is observed after nucleation, while the D/G' ratios remain relatively constant. These effects may relate to an enhancement of the G-band peak intensity related to a plasmonic resonance effect. For example, recent work[113] has shown that SWCNTs with low levels of Au tagging cause significant G-band peak intensity enhancement for laser excitation at 633 nm which corresponds to the excitation wavelength used in the present experiments. At higher fluence, there are increased D/G and D/G' ratios for the KAuBr\textsubscript{4}(aq)-exposed samples as compared to the irradiated-only SWCNTs. The relative enhancement of the D band with fluence may be attributed to a plasmonic enhancement of this mode[114] resulting from selective Au-NP nucleation at defect sites. In addition, Figure 15b shows a suppression in the charge transfer effects from the ionic dopant SWCNT samples irradiated at higher fluence and exposed to KAuBr\textsubscript{4}(aq). The presence of a considerable number of Au-NPs on the surface (as shown in Figure 14) at the high fluence does not cause additional Raman shifts, but converge at the same G'-band peak position as the irradiated-only SWCNTs indicating that the resulting Raman spectra are influenced more strongly by the defect-modulated absorption properties. The general suppression in Raman peak intensity at
higher fluence is dominated by the significant attenuation in absorption intensity related to the effects that defects have on decreasing SWCNT oscillator strength.

Defect profiling by Au-NP nucleation was also investigated as a complimentary technique to Raman analysis for confirming defect annealing in irradiated SWCNTs. Annealing of ion irradiation-induced defects in metallic SWCNT thin-films has been observed in metallic and semiconducting thin films. The high selectivity of the Au-NP nucleation to regions of ion-irradiation damage may provide a method to verify annealing by comparison of Au-NP density in irradiated SWCNTs exposed to KAuBr₄ before and after annealing. This work additionally will benefit the proposed experiments concerning surface treatments, where the electrical contact will be evaluated for damaged SWCNTs. It is possible that the annealing of defects prior to metal deposition will provide a useful comparison and may have significant influence on the conduction properties of the system.

A highly purified SWCNT paper was irradiated with 150 keV ³¹P⁺ at a fluence of 5×10¹⁴ (³¹P⁺)/cm² and divided into two papers. Following irradiation, one paper was annealed in Ar/H₂ (95%/5%) for 30 minutes at 1000 °C, while the other was placed in a vacuum oven (100 °C, ~100 mTorr). Both the irradiated and the annealed SWCNT papers were exposed to 0.01 M KAuBr₄ for 30 seconds, rinsed with DI H₂O, and dried in vacuum at 100 °C for 2 hours. The samples were subsequently analyzed via SEM for analysis of Au-NP nucleation.

It has been shown by Raman analysis that significant damage is observed in SWCNT papers irradiated with 150 keV ¹¹B⁺ to a fluence of 5×10¹⁴ (¹¹B⁺)/cm². Similarly,
significant damage was also observed for electronic-type separated SWCNT thin-films irradiated with 150 keV $^{31}$P$^+$ at the same fluence. Hence the irradiation conditions applied in the current study are expected to produce a high defect density in the SWCNT paper. The annealing conditions were selected based on preliminary Raman analysis of irradiated ($5 \times 10^{14}$ ($^{11}$B$^+$)/cm$^2$) metallic thin-films, which observed recovery of D/G and D/G' ratios after exposure to various annealing conditions. A strong correlation between Raman modes and Au-NP density has been established showing that the degradation in the Raman modes tracks directly with increasing Au-NP density. Thus, for the irradiated SWCNT paper, where a high defect density is expected, then a high Au-NP density is also expected. If the Raman modes are restored under the selected annealing conditions, then it follows that a low density of Au-NPs may be expected in the annealed SWCNT paper.

Representative SEM images (50,000× magnification) of the irradiated and annealed samples after exposure to KAuBr$_4$ are shown in Figure 16. A high density of Au-NPs is observed for the irradiated SWCNT paper (see Figure 16a), while the irradiated and annealed portion shows virtually no Au-NP nucleation (see Figure 16b). These preliminary results indicate that the Au-NP nucleation techniques enable rapid assessment of defect annealing, and may be used in conjunction with, or as an alternative to, Raman spectroscopy analysis for verification of defect annealing in SWCNTs.
Figure 16. SEM images at 50,000× magnification of a purified SWCNT paper irradiated with 150 keV $^{31}$P$^+$ at a fluence of $5 \times 10^{14}$ ($^{31}$P$^+$)/cm$^2$ and exposed to 0.01M KAuBr$_4$(aq) for 30 seconds before (a) and after annealing (b) in Ar/H at 1000 °C for 30 min.

Preliminary results indicating the usefulness of spatial defect profiling to verify annealing motivate further study and understanding of the healing process and its effect on the Au-NP nucleation phenomena. Future experiments may include exploration of different annealing conditions (i.e., temperature, time, ambient) and their effect on the Au-NP nucleation in irradiated SWCNT bulk papers and thin films.

4.4 Conclusion

An electroless Au-NP nucleation process (with KAuBr$_4$(aq)) has been rigorously characterized to identify the spatial distribution of defects in SWCNT materials after ion irradiation with 150 keV $^{11}$B$^+$. The selectivity of Au-NP nucleation onto ion-irradiated SWCNTs (and not onto purified SWCNTs) shows that the technique can also be used as
a method to controllably deposit metal nanoparticles onto SWCNTs for other applications. The nucleation of Au-NPs has been statistically analyzed as a function of exposure time at constant fluence. Short exposure time (e.g., 30 seconds with 0.01M KAuBr₄(aq)) represents a rapid, controlled approach to achieve a narrow distribution of Au-NP radii. In addition, the 30 second exposure time is sufficient to achieve equivalent particle density based on the number of available sites for nucleation from the irradiation condition, while also preventing considerable particle coalescence as observed with longer exposure times. Au-NP nucleation onto SWCNT papers with increasing ¹¹B⁺ fluence shows increasing particle density and a decrease in inter-particle distance along individual SWCNT bundles. The observed increase in Au-NP density correlates directly with an increase in the Raman peak ratios of the D and G' bands, thus providing another probe of ion-generated vacancies in SWCNTs. Raman spectral analysis on purified and ion-irradiated SWCNT papers exposed to KAuBr₄(aq) clearly show the charge transfer interactions as well as various shifts associated with defect-modulated properties from ion-irradiation and Au-NP nucleation. The technique was additionally applied as a binary indicator of defect healing in ion irradiated SWCNTs. It was observed that recovery of the D/G values from Raman analysis corresponded with a complete suppression of Au-NP deposition in the SWCNTs. Overall, the process for Au-NP deposition is amenable to standard laboratory or cleanroom practices, which may be attractive for certain nanoelectronic/sensor devices, and SWCNT papers emerge as a fluence-dependent dosimetry material. Since the SEM analysis and Raman spectroscopy probe predominantly the surface of the sample (typical penetration is ~400 nm for these
samples), the process may best be described in the future using scattering cross-section theory.
5 Modification of CNT-Ag Interface via Ion Irradiation

5.1 Introduction

The electrical and physical properties of CNT-metal interfaces are strongly influenced by electronic-type, network density, and pre/post metal deposition surface modifications. For device applications, much of the work to date has shown that SB-free contacts can be made to single SWCNTs with larger diameters (>1.7 nm) using metals with appropriate work functions. However, some applications will benefit from small diameter SWCNTs with larger band-gaps (i.e. 1 eV vs 0.4 eV), which result in better on-off ratios in FETS[23] and a broader range of band-gaps to tune to the solar spectrum for solar cell devices.[115] Even with the recent progress toward advanced metal contacts to CNTs, the contact resistance is still the dominant issue in scaled devices. According to a review published by Franklin[116], “Creative solutions have been presented for potentially addressing the creation of high-quality dielectric interfaces, but there has been much less progress on improving the contact metal interfaces. Regardless of whether a nanomaterial transistor is for high-performance or thin-film application, the device will depend heavily on the quality of transport at the source and drain metal contact interfaces.” Thus, further studies concerning contact resistance between various metals and CNTs, and the impacts of environmental factors on those properties, are necessary for further progress in the field.

As addressed previously, many studies have investigated the effects of ion irradiation on a wide range of SWCNT materials, including SWCNT papers[81, 90], electronic-type-
separated[83] and diameter controlled[117] SWCNTs thin films, and many other SWCNT types and form factors[41, 50, 82, 97, 118], yet no studies have specifically investigated the role that SWCNT-metal contacts play in measured results. In particular, ion irradiation-induced defects at the metal-SWCNT interface have yet to be examined, which is relevant for modification of the interface electrical properties and practical deployment in space and harsh environments. There is a pressing need to understand how defects influence the SWCNT-metal interface since it is becoming the dominant factor limiting performance in scaled, high-performance devices. It has recently been shown that defects or functionalization can enhance metal interactions with graphene, in terms of electrical and bonding interactions.[119, 120] However, it is not clear whether the introduction of defects through ion irradiation will result in enhancement or degradation of the CNT-metal interface properties.

In the work presented here, modification of the metal-SWCNT interface by exposure to ion irradiation is investigated. A method has been developed to determine whether ions impact the contact resistance and other electrical transport properties at the SWCNT-metal interface. There were a number of different incident ion species, as well as many different metal contacts that could be chosen for these experiments. Ag was chosen for the present experiments because other work (discussed in chapter 6) was also being performed investigating the mechanical and electrical properties of CNT-Ag composites. Figure 17 shows a plot of the projected range of different ions (in Ag) versus incident ion energy, with the energy of incident ions varied from 10 keV to 500 keV. Clearly the longitudinal range of an incident ion depends on the energy and mass, with the heavier elements experiencing more collisions and scattering, thus limiting penetration depth into
the Ag. The plot shows that the penetration depth of the chosen ions into Ag can range from less than 10 nm to over 1 micron (for protons). For the present experiment, 150 keV \( ^{11}\text{B}^+ \) was chosen for two primary reasons: (1) The penetration depth of 150 keV \( ^{11}\text{B}^+ \) in Ag is \( \sim \)184 nm, which is important because typical metal contacts to scaled devices are usually less than \( \sim \)100 nm and (2) other work such as that described in chapter 4 was done with 150 keV \( ^{11}\text{B}^+ \), thus enabling comparison of the results to previous work. Different Ag contact thicknesses have been deposited on SWCNT films to provide a means to control the ion irradiation induced damage at the metal-SWCNT contact using 150 keV \( ^{11}\text{B}^+ \), either stopping them within the Ag contacts or allowing the ions to penetrate fully through to the underlying SWCNTs. Transfer length method (TLM) measurements and analysis are used to quantify changes in contact resistance, transfer length, and specific contact resistance in response to ion irradiation. These observations along with computer simulations provide an understanding of how the defect generation within the structures affects the properties of the metal-SWCNT interface.
5.2 Experimental Methods

Structures were fabricated for performing transfer length method (TLM) measurements to extract the Ag-SWCNT contact resistance. In this study, high purity SWCNT materials were synthesized in-house by laser vaporization, purified, and thin films of this material were fabricated and prepared on Si/SiO₂ substrates using the MCE film transfer method[16, 121]. Ag contacts with thicknesses of 1.5 μm (thick contacts) and 0.1 μm (thin contacts) were deposited via thermal evaporation (Kurt Lesker PVD 75C) through a shadow mask. Figure 18a shows a schematic detailing a top-down view of the surface of the TLM structure, with Ag contact dimensions of 2 mm × 8 mm (L × 76
and SWCNT channel lengths \((d_1 – d_4)\) of 1, 2, 3, and 4 mm. The samples were irradiated with 150 keV \(^{11}\)B\(^+\) (Varian 350D medium current ion implanter) at \(5 \times 10^{14}\) ions/cm\(^2\) with the shadow mask still in place to serve as a self-aligned radiation shield for the SWCNTs in the channel regions. Figure 18b and Figure 18c illustrate this process for the thick and thin contact structures, respectively. The shadow mask is of sufficient thickness (0.5 mm) to mask the SWCNTs in the channel (between the Ag contacts) from the incident ions, so that only the Ag contacts are irradiated. Contact resistance measurements were acquired before and after ion irradiation to monitor changes in the contact resistance in response to ion irradiation. The TLM measurements were performed by forcing current between each pair of electrodes and monitoring the voltage, and the resistance calculated from the resulting values via Ohm’s law. Raman spectroscopy of the SWCNTs was performed both in the channel (shielded from irradiation) and under the contacts. Kapton tape was used to peel the Ag contacts off of the SWCNTs to enable Raman measurements of the SWCNTs under the contacts.
Figure 18. (a) Schematic showing a top-down view of structures fabricated for transfer length method (TLM) measurements of contact resistance between Ag contacts (labeled 1-5) and SWCNT thin films, with contact lengths $L$ and widths $W$ of 2mm and 8mm, respectively, and electrodes spaced a distance $d$ apart. Cross-sectional views showing TLM structures with (b) thick (1.5 µm) and (c) thin (0.1 µm) Ag contacts during ion irradiation, with the TLM shadow mask in place so that the channel region is shielded and the 150 keV $^{11}$B$^+$ are only incident on the Ag contacts.

5.3 Contact Resistance and Structural Defect Analysis

The Ag contact thicknesses were specifically chosen for two intended scenarios: (1) the ions come to rest within the thick contacts, and (2) the ions are transmitted through the thin contacts into the SWCNT film and SiO$_2$. The range of ions in metals will vary depending on factors such as the ion species, energy, and metal type. SRIM
software[107] was used to calculate the range of 150 keV $^{11}$B$^+$ in Ag (conditions for the present experiments), to ensure that the proper Ag contact thicknesses were selected. The projected range of $^{11}$B$^+$ in Ag is approximately $0.18 \pm 0.09$ µm. Thus, thin Ag contacts of 0.1 µm and thick Ag contacts of 1.5 µm were deposited to meet the given criteria of contacts either below or well above the projected $^{11}$B$^+$ range, respectively. Such an experimental setup ensures that changes in contact resistance after irradiation can be distinguished as resulting from either ion-induced damage in the Ag or ion-induced damage in the SWCNT film. Furthermore, by determining $R_C$ for both structures before and after irradiation, each structure acts as its own control sample, eliminating any speculation about differences between values based on testing of different samples.

![Graph showing I-V sweep on Ag-SWCNT contact.](image)

Figure 19. Representative I-V sweep on Ag-SWCNT contact, which is performed for each 4-point resistance measurement during the TLM characterization of the Ag-SWCNT structures.
TLM measurements of the structures described in Figure 18 were performed before and after ion irradiation to discern whether ion irradiation has any impact on the \( R_C \) of the Ag-SWCNT structures. For each measurement a full voltage sweep is performed to ensure that the results are not current or voltage dependent. The I-V plot in Figure 19 shows linear current-voltage characteristics resulting from the Ohmic contact to the sample, with an \( R^2 \) value of 1. The results of the TLM measurements are shown Figure 20, where the electrical resistance is plotted versus contact spacing for the Ag-SWCNT structures with thick and thin Ag contacts (Figure 20a and b, respectively). The closed black squares are the measured resistance before ion-irradiation, and the open red squares are the measured resistance after ion-irradiation, with dotted lines corresponding to linear least square fits to each data set (all linear fits exhibit \( R^2 > 0.996 \)). The linear fit to TLM measurements is used to determine the unknown variables by equation 1[55]

\[
R_{\text{total}} = \frac{R_{SH}}{W} d + 2R_C
\]

where \( R_{SH} \) is the sheet resistance between the contacts, \( W \) the width of the contacts, and \( d \) the distance between consecutive contacts, as defined in Figure 18. The slope of the line is directly proportional to the sheet resistance and the vertical intercept (resistance value at zero electrode spacing) is \( 2R_C \). Previous work has shown that SWCNTs irradiated under the present 150 keV \(^{11}\text{B}^+\) conditions should exhibit a fluence-dependent increase in \( R_{SH} \)[83]. No appreciable changes are observed in the slope of the linear fits to the data (and hence, \( R_{SH} \)) after ion irradiation, indicating that the SWCNTs in the channel were well shielded and that the shadow mask was properly aligned. As shown in Figure 20, the contact resistance is similar for both structures before irradiation: 102 kΩ-μm for the
thin-contact structures and 83 kΩ-µm for the thick-contact structures. Similar values are expected as both structures were made from the same SWCNT film and equivalent Ag deposition conditions. After ion irradiation, $R_C$ for the thick contacts remains relatively unchanged (91 kΩ-µm); however, $R_C$ increases by $\sim 4\times$ to 405 kΩ-µm for the structure with thin contacts. As noted previously, SRIM calculations show that the $^{11}$B$^+$ should stop well within the thick Ag contacts, and should be transmitted through the thin contacts to the underlying SWCNT film, as illustrated in the conceptual renderings in Figure 20c and 2d, respectively. Thus, the increase in $R_C$ after irradiation for the thin-contact structures suggests that the origin of the changes is related to modifications of the SWCNTs and/or the Ag-SWCNT interface, and eliminates the prospect of contributions from damaged Ag contacts.
Figure 20. Plots of the measured 4-point resistance versus Ag electrode spacing for TLM structures with Ag electrode thickness of (a) 1.5 μm and (b) 0.1 μm. Resistance values for the two structures are measured before (black square) and after (red squares) irradiation with 150 keV $^{11}$B$^+$ to a fluence of $5 \times 10^{14}$ ions/cm$^2$. The linear fits of the data are indicated by dashed lines. Conceptual illustrations show (c) thick and (d) thin metal contacts deposited on the SWCNT films, and depicts the boron ions (green dots) either stopping in the metal or transmitted through the metal to the SWCNTs beneath, respectively. Note: Although only 1 layer of SWCNTs is shown in the renderings, the actual SWCNT thin-films were random networks between 50 nm and 70 nm in thickness.

Characterization of changes in the SWCNT material properties can facilitate understanding of the observed changes in contact resistance of the Ag-SWCNT interface induced by ion irradiation. Raman spectroscopy was employed to evaluate structural damage in the SWCNTs under the contacts, as well as in the channel region, which was
shielded from the ion irradiation by the TLM shadow mask. The illustrations in Figure 21 demonstrate that the contacts were removed by adhering Kapton tape to the surface and peeling it back to reveal the bottom of the metal contact and top of the SWCNT film, thus allowing for Raman measurements of the irradiated SWCNT regions. Figure 21a (thick contacts) and Figure 21b (thin contacts) shows a representative cross-section view of two TLM contacts for the irradiated structures. The regions between the contacts, which were shielded by the shadow mask, are labeled “shielded region”, and the regions where the Ag contacts were exposed to radiation are labeled “under contacts”. In the case of the thick contacts, some SWCNTs adhered to the Ag; however, the Raman spectra of these SWCNTs were identical to those of the SWCNTs remaining on the substrate.

The characteristic Raman peaks of interest for SWCNTs are the D-peak (located at \( \sim 1300 \text{ cm}^{-1} \)), which is related to defects, the G-peak (\( \sim 1590 \text{ cm}^{-1} \)) indicating sp\(^2\) graphitization, and the G’-peak (\( \sim 2690 \text{ cm}^{-1} \)) corresponding to two-phonon scattering processes around the K-point[122]. Figure 21c shows the Raman spectra for the thick-contact structure after irradiation. The Raman spectra both in the shielded region and under the contacts are nearly identical, indicating no significant changes in the SWCNT structural properties as a result of ion irradiation, which is expected from the SRIM calculations of projected range. Figure 21d shows the Raman spectra for the thin-contact structure after irradiation. The Raman spectrum for the SWCNTs in the shielded region is also nearly identical to both spectra for the thick-contact structure (Figure 21c); however, the Raman spectrum under the contacts for the thin-contact structure shows significant changes in the prominent SWCNT peaks. The extent of structural damage (i.e., defect density) within the SWCNTs can be evaluated by examining relative changes in the
Raman peak ratios after ion irradiation. For the thin contact structure, \([D/G(\Phi)]/[D/G(0)]\) is 4.8, where \(D/G(\Phi)\) is the \(D/G\) peak ratio under the contacts, and \(D/G(0)\) is the \(D/G\) peak ratio in the shielded region. In comparison, nearly complete suppression of the \(G'\) peak in the SWCNTs under the contacts is observed. The \(G'\)-peak values were assigned using the maximum peak value from 2500 cm\(^{-1}\) – 2700 cm\(^{-1}\) for several scans, resulting in values of \([D/G'(\Phi)]/[D/G'(0)]\) ranging from 45 to 62. The collective Raman results indicate significant structural damage of the SWCNTs under the contacts, which correlates with the observed increase in \(R_C\) for the thin contact structure due to ion penetration through the Ag contacts.

Figure 21. Schematic illustrations showing the methods for acquiring Raman data under the contacts on (a) thick and (b) thin TLM structures. The channel region, which was shielded from ion irradiation, is labeled “shielded region”. Also shown is the removal of the contacts by Kapton tape to enable Raman measurements under the contacts. The Raman spectra for the shielded region and under the contacts are also shown for (c) thick and (d) thin contact structures.
5.4 Extended Analysis and Simulations of Ag-SWCNT Interface

There is a clear correlation of structural damage in the SWCNT film to an increase in $R_C$, but analysis of the transfer length ($L_T$) and the specific contact resistance ($\rho_c$) is needed to assess these effects as they relate to the Ag-SWCNT interface. As defined by the transmission line model, $L_T$ and $\rho_c$ are independent of the contact area and are a property of the metal-SWCNT interface. If the contact length is $>1.5 \, L_T$, and the sheet resistance under the contacts is identical to the sheet resistance in the channel (an assumption which cannot be verified), then equation 1 can be approximated as[55]

$$R_T = \frac{R_{SH}}{W} d + 2R_C \approx \frac{R_{SH}}{W} (d + 2L_T)$$

(2)

The contacts used in the present study have a length of 2 mm, ensuring the validity of equation 2, since $L_T$ is typically on the order of microns for contacts to SWCNT films. Solving equation 2 for $L_T$ leads to

$$L_T = \frac{WR_C}{R_{SH}}$$

(3)

By the definition of the transfer length, the specific contact resistance can be expressed as[123]

$$\rho_c = R_{SH} (L_T)^2$$

(4)

Thus, from the TLM data, the value of $L_T$ can be determined using equation 3, and $\rho_c$ can be determined using equation 4. However, for cases in which the sheet resistance under the contacts is modified, equation 2 is no longer valid because of the addition of an
“extra” series resistance for current in the SWCNT film under the contact traveling toward the channel, leading to an alternative expression of equation 2 as [123]

\[
R_{total} = \frac{R_{SH}}{w} d + 2R_C \approx \frac{R_{SH}}{w} d + \frac{2R_{SK}L_T}{w} \tag{5}
\]

where \(R_{SK}\) represents the sheet resistance under the contacts. For this scenario, \(L_T\) is now determined by a modified expression of equation 3 as

\[
L_T = \frac{wR_C}{R_{SK}} \tag{6}
\]

and \(\rho_c\) is determined by a modified expression of equation 4 as

\[
\rho_c = R_{SH} (L_T)^2 \tag{7}
\]

In most cases, it is not possible to know the sheet resistance under the contacts, and thus additional measurements are needed to determine \(L_T\) and \(\rho_c\). This scenario is commonly seen where modifications have been made to achieve Ohmic metal-semiconductor contacts, such as silicide contacts [123, 124]. Typically in these cases, \(R_C\), \(L_T\) and \(\rho_c\) decrease as a result of improving the contact interface. However, the present study permits a direct measurement of \(R_{SK}\) after the contacts are removed. The sheet resistance under the contacts was measured by the van der Pauw technique [125] for multiple contacts, and on average was \(\sim 22\,k\Omega/\square\). Previous work [83, 117] has shown that the relative increase in sheet resistance at a given fluence correlates linearly with the relative increase in \(D/G'\) peak ratios (i.e., \([D/G'(\Phi)]/[D/G'(0)] \approx [R_{SH}(\Phi)]/[R_{SH}(0)]\)). Thus, based on the measured \([D/G'(\Phi)]/[D/G'(0)]\) values between 45 – 62, it is expected
that the sheet resistance under the contacts should increase by 45x – 62x relative to the sheet resistance in the channel. Using the sheet resistance in the channel of 363 Ω/□ (\(R_{SH}\) shown in Figure 20b), the expected sheet resistance values are between ~16 kΩ/□ to ~22 kΩ/□, which is consistent with the measured value of ~22kΩ/□. Table 1 shows the calculated TLM values for the thin-contact samples, both before and after irradiation, and provides details of how those values are determined. Despite the increase in \(R_C\) (and significant increase in \(R_{SK}\)), the transfer length and specific contact resistance after irradiation decrease by ~15x and ~4x, respectively. The decrease in \(L_T\) and \(\rho_c\) suggests that the irradiation-induced damage improves the electrical properties of the Ag-SWCNT interface. Thus, the overall measured increase in \(R_C\) is a result of adding a series resistance between the Ag-SWCNT interface and the SWCNTs in the channel region, and this increase in resistance dominates over any potential benefits gained by electrical enhancement of the Ag-SWCNT interface.

### Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Sheet resistance (Ω/□)</th>
<th>(R_C) (kΩ-μm)</th>
<th>(L_T) (μm)</th>
<th>(\rho_c) (Ωcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>363 (^1)</td>
<td>102</td>
<td>282 (^2)</td>
<td>0.29 (^3)</td>
</tr>
<tr>
<td>Irradiated</td>
<td>22,000 (^4)</td>
<td>405</td>
<td>18.4 (^5)</td>
<td>0.075 (^6)</td>
</tr>
</tbody>
</table>

\(^1-3\) Determined from eqs 1, 3, and 4, respectively. \(^4\) Measured by van der Pauw method. \(^5,6\) Determined from eqs 6 and 7, respectively.

SRIM simulations were employed to evaluate the validity of the current observations and gain additional insight in terms of displacement damage (vacancy production) within the materials. The “Transport of Ion in Matter” (TRIM) program within SRIM was used to simulate 150 keV \(^{11}\)B⁺ collisions into a Ag/C/SiO₂ (100 nm/70 nm/250 nm) target using detailed collisions with full damage cascades, 40,000 particle histories, and
assuming a C density of 0.5 g/cm³ and displacement energy of 20 eV[117]. The non-ionizing energy loss (NIEL) was calculated based on vacancies in the carbon layer from the TRIM output files[126], and “effective NIEL” values ($NIEL_{eff}$)[83] were calculated based on a range of SWCNT film thickness of 50 nm – 70 nm as measured by profilometry. The displacement damage dose ($DDD$), which is the energy per mass lost to vacancies, is then calculated by the product of $NIEL_{eff}$ and fluence (i.e., $DDD = NIEL_{eff} \times$ fluence). Previous work with SWCNTs synthesized by identical methods established a fit relating structural and electrical degradation to $DDD$ as[117]

$$\frac{D/G'(\Phi)}{D/G'(0)} = \frac{R_{SK}}{R_{SH}} = 1 + \frac{DDD}{2.01 \times 10^{15}}$$

Hence, using TRIM simulation outputs to determine the $DDD$, in conjunction with equation 8, enables analysis of the electrical and structural degradation in the SWCNTs.

The $DDD$ values calculated from the TRIM simulations in Figure 22a show that the energy lost to C atom displacements is highest throughout the first 6 nm of the SWCNT film (sample depth of 106 nm). The energy lost continues to decrease within the first 20 nm, followed by a slight increase over the range of the film thickness (70 nm). Based on the TRIM outputs, the average $DDD$ for the full SWCNT film is $8.6 \times 10^{16}$ MeV/g, which results in a relative change of ~44 for the $D/G'$ or $R_{SH}$ values from equation 8. In comparison, the $DDD$ representing the increased damage over the first 6 nm of the SWCNTs is $1.2 \times 10^{17}$ MeV/g, which gives a relative change of ~61 for the $D/G'$ or $R_{SH}$ values. Based on the Raman results from Figure 21d, the measured range for $[D/G'(\Phi)]=[D/G'(0)]$ is 45 – 62, which is highly consistent with the simulation results.
Moreover, based on the starting sheet resistance value of 363 Ω/□ from Figure 20b, the simulation results predict an expected range of ~16 kΩ/□ to ~22 kΩ/□ for $R_{SK}$, which is in strong agreement with the measured value for $R_{SK}$ of ~22 kΩ/□. Therefore, the combination of TRIM simulation results with the $DDD$ methodology is valid for analysis of electrical and structural degradation in SWCNT-metal contact structures.

The outcome of the TRIM analysis regarding $DDD$ in the first several nanometers of the SWCNTs leads to very good agreement between predicted and measured values for $R_{SK}$, yet does not explain the physical mechanism for the enhancement of $L_T$ and $\rho_c$ at the Ag-SWCNT interface. The cause of increased displacement damage at the interface can be better understood by analysis of the incident $^{11}$B$^+$ and recoil distributions in the SWCNT layer. Figure 22b shows the distributions of B ions, and final location of Ag and C recoils vs. depth into the sample, which reveals a high distribution of forward-scattered Ag (relative to C and $^{11}$B$^+$) in the first 4 nm (sample depth of 104 nm) of the SWCNT film. Multiplying any ion/recoil distribution by the dose ($5 \times 10^{14}$ ions/cm$^2$) gives an atomic density distribution (i.e., atoms/cm$^3$), which can be converted into an atomic ratio by dividing by the total atomic density of the layer. Interestingly, from 100 nm to 104 nm (4 nm into the C layer), the average Ag concentration is $9.2 \times 10^4$ ppm (or 9.2%), decreases dramatically for depths greater than 12 nm in the SWCNT film (sample depth > 112 nm). In contrast the $^{11}$B$^+$ concentration is < 50 ppm throughout the Ag and SWCNT layers; the C concentration in the Ag layer is also < 50 ppm, except at a sample depth of 95 nm to 99 nm (directly before the Ag-SWCNT interface) where the concentration is ~245 ppm due to backscattered C. The analysis of the ion and recoil distributions reveals that forward scattered Ag atoms are responsible for the significant displacement damage.
at the Ag-SWCNT interface, but also suggest the existence of an Ag/C (9%/91%) interfacial layer with improved electrical interactions with the Ag contacts. The overall results suggest that under the present irradiation conditions, the use of SWCNT active layers approaching monolayer thickness may lead to a reduction in $R_C$ values as a result in the enhancement of $L_T$ and $\rho_c$ at the Ag-SWCNT interface. This is consistent with recent work on modified graphene-metal contacts, where defects from O$_2$ plasma etching decreased the overall contact resistance[120]. Alternatively, subjecting structures with thicker SWCNT films (i.e., > 20 nm) to a lower dose of ion irradiation may achieve similar improvements, provided that the ion fluence is below a significant displacement damage threshold. The implication of the work is a potential method to enhance the electrical properties and improve the contact resistance of metal-nanocarbon interfaces via ion implantation, which is advantageous from a device processing perspective, as it is performed after metal deposition, eliminating the need for exposure of modified or functionalized SWCNTs to the atmosphere.
Figure 22. Results of TRIM simulations for 150 keV $^{11}$B$^+$ into a Ag/C/SiO$_2$ (100 nm/100 nm/250 nm) target showing (a) displacement damage dose (DDD) plotted as a function of depth in the SWCNT (carbon) layer, and (b) $^{11}$B$^+$, Ag recoil, and C recoil distributions plotted versus depth into the Ag and SWCNT layers.

5.5 Conclusions

The effects of ion irradiation on the Ag-SWCNT interface has been studied, and results show that exposure to extreme ion irradiation can significantly impact the electrical properties of metal-SWCNT contacts. The contact resistance of structures irradiated with $5 \times 10^{14} \text{ } ^{11}\text{B}^+/\text{cm}^2$ increased by 4x for structures with thin Ag contacts (0.1 µm), and did not change for structures with thick Ag contacts (1.5 µm). The changes in $R_C$ are directly correlated to structural damage in the SWCNTs as confirmed by Raman spectroscopy measurements. However, sheet resistance measurements under the contacts in conjunction with transmission line model theory indicate that the electrical interactions of the Ag-SWCNT interface are improved, as evidenced by a decrease in transfer length.
and specific contact resistance of 15x and 4x, respectively. This infers that transport in the Ag-SWCNTs has actually been improved by the ion irradiation, while transport through the SWCNTs has been degraded. SRIM analysis reveals that the highest displacement damage occurs at the contact interface, beneath which the SWCNTs are still highly (but slightly less) damaged. Analysis of the ion and recoil distributions suggests that damage at the Ag-SWCNT interface is caused by forward scattered Ag atoms, which may explain the improvement in the electrical properties of the Ag-SWCNT interface despite significant damage. It is thus proposed that the increase in contact resistance observed for the thin-contact structures is purely a result of increased series resistance of the SWCNT film between the Ag electrodes and the SWCNTs in the channel region, suggesting that exposure to lower ion fluence or utilizing very thin SWCNT films may result in improved $R_C$ values as well. Thus, for metal contacts to SWCNT films $>$20 nm thick exposed to extreme ion irradiation conditions, metal contact thickness will be an important consideration for proper shielding of the metal-SWCNT interface. Conversely, for thinner SWCNT materials or less extreme ion irradiation conditions, $R_C$ may actually improve as a result of ion irradiation exposure.
6 Carbon Nanotube Metal Matrix Composites

The following section summarizes the efforts regarding development of carbon nanotube metal matrix composite electrodes, including processing and fabrication, mechanical testing, and electrical testing under stress. Portions of this section contain excerpts from 2 publications:


6.1 Introduction

Enhancing the strength, ductility, and other mechanical properties of metal thin films would be beneficial to a variety of applications, including solar cells and flexible electronics[127]. For instance, micro-cracks have been shown to cause decreased power output in single- and multi-crystalline Si PV modules [128-130]. Triple junction solar cells used in space applications have experienced fracture issues, with 10% of the cells on spacecraft arrays requiring replacement pre-launch[131]. Recently, a new solar cell technology (Inverted Metamorphic Multijunction - IMM) has been developed that offers both higher efficiency and dramatically reduced mass[132] as compared to traditional III-
V solar cells, with significant potential for both space[133] and terrestrial concentrator[134] applications. These advanced solar cells, slated to replace triple-junction cells, are thinner and much more fragile, and will likely be even more susceptible to fracture damage[135]. Cracks in solar cells cause loss of active cell area when a fracture propagates through the contact metallization, electrically disconnecting large portions of the cell. Thus, it is important that strategies be investigated to develop more robust metal electrodes.

A possible approach for attaining more robust electrodes is to replace the traditional thick silver conduction layer with a metal matrix composite (MMC) film that will have the needed combination of mechanical integrity (ductile matrix metal) and redundant electrical conduction paths to assure no loss in electrical connectivity due to cracks in the underlying solar cell. A MMC consisting of conductive fibers in a metal matrix can conduct electricity, even if the matrix is stressed to the point of fracture, provided the conductive fibers remain in electrical contact to both sides of the fracture. CNTs are an attractive option for a reinforcement material as they are strong, flexible, conductive, and have been used as reinforcement in bulk metal matrix composites (MMCs) and coatings to increase yield strength[136], hardness[137, 138], and wear resistance[139, 140].

The field of metal matrix composites (MMCs) has a long-standing history, yet the recent and continual development of new nanomaterials provides additional opportunities for its expansion. Carbon nanotubes have mechanical properties that make them an attractive option for reinforcement material, in terms of both tensile strength[7] and their high strain capabilities in response to applied stress[141]. The main challenges in
fabricating CNT-MMCs are achieving homogeneous dispersions of CNTs in the metal matrix, high surface tension between most metals and CNTs resulting in low interfacial bond strength, and chemical/structural stability of the CNTs in metals processing. Much work regarding MMCs reinforced by CNTs has focused on developing bulk MMCs or thin-film coatings for wear resistance. There has been little work done to assess the viability of thin film MMCs for use as a conducting electrode. Mechanically reinforced electrodes could be beneficial to a number of applications, including solar cells and flexible electronics and provide an interesting opportunity to both develop CNT-MMC thin film fabrication techniques and study the CNT-metal interactions. There are a number of methods for fabricating MMCs, including powder metallurgy[136, 139, 142], thermal spraying[137, 143, 144], electrochemical deposition[145, 146], melting and sintering[147, 148] and physical vapor deposition for layer-style (sandwich) processing. Some of these methods (powder metallurgy, melting, and thermal spraying) are not practical from a solar cell or flexible electronics processing perspective because of the high temperatures/pressures needed for fabrication, and additionally may be difficult to implement as a method to controllably deposit thin films with specific thickness requirements. It is still very difficult to make thin film MMCs in which CNTs are well dispersed. Consequently, layer-style processing using PVD techniques (e-beam, thermal, sputtering) may yield interesting new results. Layered processing in which CNTs are embedded between deposited metal films is a technique that “few research groups have investigated”, according to a review of carbon nanotube reinforced metal matrix composites[149]. Thus, investigating techniques to fabricate layered thin film MMCs could be valuable, and provide opportunities to investigate the effects of the CNT layer
thickness on the metal morphology and mechanical properties of the MMCs. In particular, the appropriate CNT film morphology and thickness needs to be identified to create composites which are truly reinforced and continuous, as opposed to composites that are simply discrete layers of metal and CNTs. Strategies for measuring the mechanical performance and properties of the CNT MMCs will also be necessary for demonstrating the utility of such structures to semiconductor and flexible electronics applications which require more robust electrodes.

6.2 MMC Fabrication Process Development

6.2.1 Preliminary Experiments

The layered or “sandwich” style process, in which CNTs are embedded between evaporated Ag layers, was utilized for all MMC experiments. This process was chosen because of solar cell and flexible electronics process compatibility, and because of the opportunities for development discussed in chapter 6.1. There are a number of CNT deposition techniques that could be useful in the layer-style processing, including thin-film transfer, ultrasonic spraying, and drop-casting. Additionally, different types of nanomaterials could be useful and may have select advantages as reinforcement materials, including SWCNTs, MWCNTs, Ag nanowires, or even hybrids of these materials. For instance, SWCNTs have the most attractive electrical and mechanical properties, while MWCNTs are typically longer and can be as little as one-hundredth the cost of SWCNTs.
Initial experiments were conducted to attain proof-of-concept, showing that SWCNTs could be an effective crack-bridging reinforcement option. Thermal evaporation of Ti/Ag (5nm/250 nm) was performed on 175 µm thick semi-insulating (100) GaAs substrates through a shadow mask. The native oxide was removed by HCl immersion immediately before the deposition process. Following deposition, drop-casting of purified laser SWCNTs was performed onto the silver. The SWCNTs were dispersed in dimethylacetamide (DMA) at a concentration of 0.6 µg/mL via bath sonication for 2 hours, and were then pipetted onto the GaAs substrates at 120 °C on a hotplate. Drop-casting was followed by thermal oxidation in a muffle furnace at 300 °C for 2 hours to remove solvents and other residuals from processing. Another thermal evaporation of Ag (350 nm) was performed to topcoat the SWCNTs and create a Ti/Ag/SWCNT/Ag composite structure. The sample was mounted on carbon tape on an SEM sample stub and intentionally fractured with stainless steel tweezers. When observed by SEM following the fracture, images were acquired of both the Ag/SWCNT/Ag interface (Figure 23a), and gaps above the fracture lines (Figure 23b). The Ag/SWCNT/Ag interface clearly shows the edge of the fracture and that the SWCNTs have remained in the metal matrix despite the high stress of fracture. Additionally, images of the fracture revealed areas in which gaps as large as 3 µm long were bridged by SWCNTs. This represents an important step as proof that SWCNTs can physically bridge large gaps over a fractured substrate.
6.2.2 MMC Fabrication and Metal Morphology Analysis

The drop-casting method described in the preliminary experiments demonstrated the crack bridging capabilities of SWCNTs, but there are inherent difficulties in the process that make this option less desirable. As the solvent evaporates the solution drops below the dispersion limit (~5 µg/mL) and the SWCNTs begin to re-bundle and will tend to agglomerate in certain areas. This is undesirable because for reliable SWCNT-metal composites the SWCNTs need to be uniformly distributed on the Ag base coat, in order to ensure that SWCNTs will be present to bridge any tensile cracks or fractures regardless of where they form. Thus, SWCNT thin film deposition by MCE transfer was utilized for further experiments to avoid agglomeration and provide a uniform CNT layer. Another
benefit of the film deposition process, besides uniformity, is the fact that the thickness of the SWCNT film can be varied and easily controlled by controlling both the volume and concentration of the starting dispersion prior to filtration onto the MCE filters.

Experiments were conducted with SWCNT films of varying thickness to determine the appropriate SWCNT weight loading for creating robust MMC structures. Test structures were prepared by first depositing a Ti/Ag (6 nm/500 nm) base-layer on a GaAs wafer via thermal evaporation. Prior to the thermal evaporation the native oxide on the GaAs wafer was removed by soaking in HCl. SWCNT films were deposited onto the Ag base-layer by the standard MCE transfer process. The resulting sample was purified through thermal oxidation at 300°C in air for 2 hours. An additional 500 nm of silver was thermally evaporated over a portion of the SWCNT thin-film and Ag base-layer. The thickness of the SWCNT films was adjusted by varying the mass of the SWCNTs, creating films with different areal densities. For instance, an areal density of 10 µg/cm² corresponds to ~100 nm thick SWCNT film, as measured by profilometry. Initially, 10 µg/cm² and 30 µg/cm² SWCNT films were used to fabricate the MMCs. A cross-section of the MMC structures shown as the inset in Figure 24 allows for analysis of the Ag top-layer morphology in relation to both the SWCNT film (left of dash) and the underlying metal (right of dash). SEM analysis of the Ag top-layer over the 10 µg/cm² SWCNT film is shown in Figure 24a, wherein the observed Ag grain structure is small, with many discrete particles. The Ag grain structure over the 30 µg/cm² SWCNT produced nearly identical results. In contrast, Figure 24b shows the SEM results of the Ag top-layer deposited directly onto the Ag base-layer, which has much larger grain structure compared to the Ag deposited onto the SWCNTs. The observed difference in grain
structure based on the underlying substrate suggests that there is little interaction between the Ag top-layer and the Ag base-layer over the SWCNT films. These observations motivate further understanding of the effect of the SWCNT film thickness on the final metal grain structure. It is unknown at this time whether a harder film (more grain boundaries) or a more ductile film (continuous) is desirable during a fracture event.

Figure 24. SEM images at 50,000× magnification show the Ag top-layer (a) over the SWCNT thin film (10 µg/cm²) and (b) over the Ti/Ag base-layer. The inset figure is a cross-section of the MMC.

It is presumed that if the SWCNT film is sufficiently thick, then the Ag-SWCNT-Ag composite will exhibit discrete layers, and upon substrate fracture these discrete layers may delaminate due to stress at the film interfaces. Some delamination was observed at the SWCNT interface in the initial test structures for SWCNT film thicknesses of 30 µg/cm². It is thus imperative to determine the optimal areal density of SWCNTs necessary for reinforcement, rather than discrete layers. Reinforcement implies that the
SWCNT network is sufficiently thin and porous to allow the Ag top-layer to penetrate through the SWCNT network and nucleate both on the SWCNTs and the Ag base-layer, thus forming a continuous structure. The concepts of reinforced and discrete layer regimes are illustrated graphically in Figure 25.

Figure 25. Conceptual rendering showing the difference between reinforcement and discrete layer regimes in sandwich-style CNT-metal matrix composite structures.

Five SWCNT thin-films, with areal densities of 1 µg/cm², 2 µg/cm², 5 µg/cm², 10 µg/cm², and 30 µg/cm², were prepared and transferred onto the Ti/Ag base-layer using the standard MCE transfer method. The thicknesses of the SWCNT films corresponding to are approximately 10 nm, 20 nm, 50 nm, and 100 nm, as estimated based on profilometry measurements. Scanning electron microscopy (SEM) analysis was employed to gain a qualitative assessment of the thin-film morphology, silver grain structure, and MMC quality. The schematic in Figure 26 depicts the fabrication processing steps.
Figure 26. The schematic depicts samples processed with the Ti/Ag (10 nm/500 nm) base-layer thermally evaporated on GaAs, SWCNT thin-film deposition, thermal oxidation at 300°C for 2 hours, followed by thermal evaporation of the Ag (500 nm) top-layer.

Figure 27 shows representative SEM micrographs corresponding to each SWCNT thin-film areal density used in the experiment. The larger grain size and reduced grain boundaries for the Ag deposited on 1 µg/cm², 2 µg/cm², and 5 µg/cm² SWCNTs (Figure 27 b, c, and d, respectively) is immediately apparent compared to the 10 µg/cm² and 30 µg/cm² sample (Figure 27 e and f). Qualitative analysis of the three samples with the lowest areal density consistently shows that the 1 µg/cm² sample exhibited the largest Ag grain size, closely resembling the grain structure of the Ag-only control samples; however, the 2 and 5 µg/cm² samples are very similar. It is evident from these differences in metal morphology that the SWCNT surface has an impact on the grain structure of the
over-coated Ag. These qualitative observations of Ag grain structure can be quantified by particle size analysis in *ImageJ*.

![Image of SEM images](image)

**Figure 27.** The SEM images at 50,000× magnification show the Ag grain structure for the 500 nm Ag top-layer deposited onto SWCNT thin-films with areal densities of (a) 0 µg/cm² (Ag control) (b) 1 µg/cm², (c) 2 µg/cm², (d) 5 µg/cm², (e) 10 µg/cm², and (f) 50 µg/cm².

Analysis of the micrographs in Figure 27 was conducted using *ImageJ*. The *FFT bandpass filter* function was used to sharpen the images, and *thresholding* was applied between 70 and 255 digital counts to highlight the individual grains. The *particle analyzer* function was used to obtain grain size distributions. The grain size was determined by calculating the diameter of each Ag grain based on the measured area (assuming a circular geometry). The results are shown in Figure 28, and corroborate the qualitative observations concerning the Ag grain structure. Based on this analysis, it is proposed that the discrete layer regime occurs at SWCNT loadings ≥ 10 µg/cm². However, measurement of other material properties may be necessary to more accurately
determine the crossover between reinforcement and discrete layers. It is not presently understood why the dramatic grain structure change between 5 and 10 µg/cm² occurs. One possibility is that the change is related to interactions of the Ag with the substrate, because of the similarities between the thinner samples. The grain structure is largest for the thinnest SWCNT sample, which implies the Ag may more effectively penetrate through the network to the base-layer, thus increasing the contributions of the base-layer to the overall grain structure. As the thickness increases, the effect of the SWCNT morphology on the final grain structure also increases.

![Figure 28. The results of imageJ analysis of the Ag grain diameter as a function of SWCNT film areal density.](image)

Figure 28. The results of imageJ analysis of the Ag grain diameter as a function of SWCNT film areal density.
6.3 MMC Mechanical Characterization

In addition to correlating mechanical properties of MMCs to the grain structure analysis discussed in chapter 6.2.2, it is additionally important to demonstrate improvements in mechanical properties of the MMCs compared to traditional Ag electrodes. Investigation of the mechanical performance of thin film MMCs has been limited, due to difficulty in preparing and testing samples by conventional methods. Previous research dedicated to this topic often employs complex methodology for fabricating and/or testing free-standing thin films because of difficulties associated with handling and clamping the delicate samples for tensile tests [150-154]. Therefore, improved fabrication methods which enable measurement of traditional stress-strain relationships in metallic thin films can also aid in characterization of advanced MMC concepts.

The present chapter describes a streamlined process for producing free-standing metallic films that enables traditional dynamic mechanical analysis. The process was also adapted to create layered thin film MMCs by embedding SWCNTs between two Ag layers, and the SWCNT weight loading has been systematically varied to improve mechanical properties of the MMCs as compared to Ag-only films.

Ag control samples and Ag-SWCNT MMCs were fabricated as free-standing films (FSFs) for tensile testing. PVC tape was mounted onto a glass slide and laser-cut to create a dog-bone patterned mask (Figure 29a). Ag was deposited at a thickness of 1.5 μm over the PVC mask via thermal evaporation, and the mask was subsequently removed (Figure 29b). For the Ag control samples, an additional 1.5 μm Ag was deposited over the base-
layer in a second deposition step. MMC samples were prepared by transferring high purity SWCNT films onto the Ag base-layer (using a previously described method[121]) and were subsequently over-coated with an additional 1.5 μm Ag.

Both the Ag control and MMCs were released from the substrate by partial liftoff of one end of the dog-bone structure from the glass with Kapton tape (Figure 29c). The tape was attached to a small Kapton film “anchor” (Figure 29d), which prevents the structure from curling up due to stress and alleviates issues related to handling/clamping the films for tensile testing. These steps were repeated at the opposite end of the structure to fully release it from the glass slide, thus creating a FSF (Figure 29e).

The SWCNT loading in the MMCs was varied by depositing SWCNT films of varying areal densities including 1, 2, and 5 μg/cm², corresponding to film thicknesses 10, 20, and 50 nm, respectively. Film thickness was measured by contact profilometry using a Tencor P2 Profilometer. These SWCNT weight loadings were chosen based on the previously proposed region of reinforcement based on initial grain structure analysis. However, the grain structure analysis needs to be repeated since the substrate (glass) and Ag layer thicknesses (1.5 μm) are different than those in the initial experiment. The Ag layer thickness was increased to more closely mimic the typical electrode thicknesses used in space solar cells, which is usually ~3 - 4μm.

The Ag grain structure of each FSF was characterized by scanning electron microscopy (SEM). The mechanical properties were quantified by tensile testing using a TA Instruments Q800 dynamic mechanical analyzer at room temperature, by clamping
the Kapton anchors and pulling in opposite directions at a constant strain rate of 0.05 %/min until failure.

Figure 29. Photographs showing the fabrication steps for creating free-standing thin films. (a) Dog-bone structures are laser-cut into PVC tape mounted on a glass slide, followed by (b) thermal evaporation of Ag and removal of the sacrificial PVC. (c) Kapton tape is used to peel up one end of the structure and (d) is attached to a Kapton film “anchor”. (e) The free-standing film is fully released from the substrate by repeating steps c and d

Tensile testing of each Ag and MMC FSF was performed to assess potential benefits of incorporating SWCNTs into the Ag matrix in terms of strength and/or ductility. The representative stress-strain curves resulting from tensile testing of the constructed sample set of FSFs with increasing SWCNT loading are shown in Figure 30a. The results clearly show that the addition of SWCNTs to the Ag matrix changes the response to applied stress. Figure 30b shows the ultimate tensile strength (UTS) as a function of SWCNT
layer thickness. The UTS increases from 243 MPa for the Ag control sample to a maximum value of 315 MPa for the MMC with 20 nm SWCNT film thickness, which is followed by a marked decrease in UTS for the highest SWCNT loading. Figure 30c shows the strain-to-failure as a function of SWCNT loading, which is similar to, yet more pronounced than the UTS trend. The strain-to-failure for Ag control is 1.1%, which increases by ~2x with a 20 nm SWCNT layer, and again decreases at a 50 nm SWCNT layer thickness. The UTS and strain-to-failure for the Ag control are comparable to similar Ag films described in other work, which were fabricated and measured by more complex techniques[154]. The improvements in UTS for the MMCs are attributed to the high intrinsic strength of individual SWCNTs which have been shown to be ≥ 20 GPa[7]. The improvement in strain-to-failure is likely due to a combination of elastic strain for individual SWCNTs (reported to be as high as 5.8%[141]) and some reorientation of the random SWCNT network under stress. The collective improvements in mechanical properties are best expressed in terms of toughness, as this metric incorporates aspects of both strength and strain. Toughness values are calculated as the integral of the stress-strain plots in Figure 30a, and are shown as a function of SWCNT loading in Figure 30d. The toughness increases from 1.66 MJ/m$^3$ for the Ag film to a maximum of 4.13 MJ/m$^3$ with incorporation of 20 nm SWCNT films, which is followed by a dramatic decrease in toughness for the MMC with 50 nm SWCNT layer thickness. Based on the measured increase in mechanical performance up to 20 nm SWCNTs (2µg/cm$^2$), it is likely that the SWCNTs are providing reinforcement in the MMCs. Reinforcement is expected to occur when the top-layer of Ag penetrates through the SWCNTs to the Ag base-layer, creating a continuous structure. The structure with 50 nm SWCNT layer (5µg/cm$^2$) shows a
reduction in mechanical properties compared to Ag in all cases, which suggests that the structure consists of discrete layers where the overall performance is dictated by the individual layers in response to an applied stress. Therefore, from a mechanical perspective, there is a clear benefit to utilizing SWCNTs as a reinforcement in MMC thin films, as evidenced by the 2x increase in strain-to-failure and ~2.5x overall increase in toughness. The results also suggest that the mechanical properties could be further improved with increased SWCNT loading by incorporating multiple thin SWCNT layers within the MMCs.
Figure 30. (a) Plots of stress versus strain for Ag control and MMC free-standing films with SWCNT layer thicknesses of 10, 20, and 50 nm. The properties of (b) ultimate tensile strength, (c) strain-to-failure, and (d) toughness are plotted as a function of SWCNT layer thickness.

SEM analysis of each FSF was performed for an assessment of the Ag grain structure, and to ascertain a possible relationship between grain structure and mechanical performance. Figure 31a-d shows SEM micrographs of the Ag surface of the FSFs characterized in Figure 30. The trend in Ag grain size was quantified with a minimum of 550 measurements for each sample with ImageJ software to determine the Martin
diameters of the Ag grains. The average grain diameter for the Ag control is ~177 nm, decreasing as the SWCNT loading increases, and beginning to level off at ~95 nm for the structure containing a 50 nm SWCNT film. The decrease in Ag grain size with increased SWCNT loading is consistent with previous observations for the structures with 500 nm Ag top layer on InP substrates mentioned in the previous chapter[155], and implies that the small grain structure at the highest SWCNT loading results in minimal interaction between the Ag top and base layers. Thus, the grain structure analysis supports the assertion that the transition from reinforcement to discrete layers occurs in structures with SWCNT layer thicknesses between 20 and 50 nm.

Figure 31. SEM micrographs of the Ag top-layer for (a) Ag control and MMC free-standing films with SWCNT layer thicknesses of (b) 10 nm (c) 20 nm, and (d) 50 nm. (e) The average Ag grain diameter as a function of SWCNT layer thickness. The labels and fading blue background indicate a transition from reinforcement to discrete layers.

Further SEM analysis was conducted to examine the fracture edge of the FSFs after being stressed to failure (Figure 32). The SWCNTs protrude more than 1 µm from the
fracture edge for the MMC samples, and the number of protruding SWCNTs increases with SWCNT layer thickness (Figure 32b-d). Additionally, the Ag top-layer delaminates for the structure containing a 50 nm SWCNT film, curling back to form a ridge along the fracture edge (Figure 32d). The delamination is not observed in the MMCs with lower SWCNT loading, further confirming the previous analysis of discrete layering occurring in the structure with 50 nm SWCNT films. The SEM analysis of the fracture edge suggests that embedded SWCNTs show strong potential to mechanically and electrically bridge micro-cracks in MMC electrodes for various applications such as solar cells and flexible electronics.

Figure 32. SEM micrographs of the fracture edges after tensile testing of (a) Ag control and MMCs with SWCNT layer thicknesses of (b) 10 nm (c) 20 nm, and (d) 50 nm. SWCNTs are shown protruding from the fracture edges.

6.4 MMC Electrical Characterization

Measuring improved electrical performance of CNT-MMCs under mechanical stress (as compared to traditional Ag electrodes) is another important step toward demonstrating the utility of the MMCs as a more crack-resistant electrode. An apparatus was built at the Air Force Research Labs at Kirtland AFB, New Mexico that measures the
electrical resistance across cleaves and cracks (or “RACK”) in order to mimic micro-crack propagation and thermal expansion scenarios. The RACK test apparatus is shown in Figure 33. The RACK testing is implemented by mounting grid finger structures on a PCB board with a fixed end, a gap, and the opposing end attached to a stage driven by a piezo-electric motor. The MMC structures are scribed and cleaved across the PCB gap and the initial crack length is measured by optical microscopy. After the crack is initiated and measured, a piezo motor is activated, slowly widening the gap in the PCB board and recording the motor position, which, when combined with the initial crack length, gives the total crack length. Load resistors (R1, R2, R3, R4) 200 Ω each are soldered to each grid finger, along with leads at the end of each grid finger and the bus bar, creating the circuit. The resistance of each grid finger is monitored for the duration of the mechanical testing until electrical failure, by monitoring the current and voltage drop across each grid finger and calculating the resistance from Ohm’s law.
Figure 33. “RACK” electrical test fixture for testing grid finger MMC test structures. The grid finger is mounted on a PCB with a fixed end, a gap, and the opposing end attached to a stepper motor. The dashed line indicates the initial crack, which is followed by motion of the “free PCB” end. Load resistors (R1-R4) and electrical leads are attached for monitoring the grid finger electrical resistance during testing.

Initial grid finger structures were fabricated for “RACK” testing to compare Ag to SWCNT-MMC electrode electrical performance. A grid finger shadow mask was designed and machined for deposition of the Ag grid finger layers. The design is shown in Figure 34a and a photograph of the final machined shadow mask is shown in Figure 34b. Following standard cleaning of the InP substrates with acetone and IPA, a Ti/Ag base-layer (5nm/500nm) was deposited through the grid finger mask. The complete sample set consisted of MMCs with SWCNT loadings of 1 µg/cm², 2 µg/cm², 5 µg/cm², and 10 µg/cm², along with Ag control samples. The SWCNT films were transferred by
the standard MCE transfer process, and a photograph of the SWCNT films on Ag are shown in Figure 35.

Figure 34. Grid finger shadow masks were designed for RACK electrical testing. (a) The design and dimensions of the grid finger mask. (b) A photograph of the finished grid finger mask.
Figure 35. SWCNT films of varying areal density deposited onto Ti/Ag grid finger base-layers for RACK electrical testing.

Ag top-layer deposition was performed subsequent to SWCNT film transfer by realigning the grid finger mask to the Ag base-layer (alignment verified by optical microscopy) and thermally evaporating 500 nm Ag through the shadow mask. At this step in the process, the MMC fabrication is complete; however, in order to create electrically isolated grid fingers, the SWCNTs between the grid fingers need to be removed. A schematic illustrating the lithography and etch process for removing the SWCNTs in the field region is shown in Figure 36. Briefly, the cross-section is shown of the MMCs with SWCNTs in the field region (between the grid fingers). The entire structure is spin-coated with photoresist (Shipley S1813) and a clear field lithography mask is exposed using a broadband mercury lamp contact aligner (Karl Suss MA56, g-
line) at 90 mJ/cm². Following exposure, the structures are developed in CD26 for 3.5 minutes, leaving the SWCNTs in the field region exposed and the grid finger portions masked by photoresist. The structures are then subjected to reactive ion etching (Drytek Quad RIE) in an oxygen plasma for 90 seconds, which etches the SWCNTs in the field region. Reactive ion etch conditions were 50 sccm O₂ flow rate, 100 mTorr chamber pressure, and 100 W RF power. It is important to note that the oxygen plasma also etches the photoresist, but calibrations of the etch rate under these conditions revealed that the SWCNTs are etched much more rapidly than the photoresist, so the Ag grid fingers remain protected from oxidation. The final step in the process is stripping the remaining photoresist from the electrodes, which is performed by soaking the structures in acetone for several minutes, followed by rinsing with acetone and IPA. The structures were shipped to the AFRL for testing following successful completions of the fabrication process.
The samples described above were mounted on the RACK and tested using the procedure outlined in Figure 33. For the initial RACK tests, all Ag samples and some of the SWCNT MMC samples failed electrically at the initial crack. This is partly due to the need to develop a more controlled substrate fracture method, as the initial crack can vary.
from 2 µm to > 6 µm. An example of RACK data for two SWCNT-MMC electrodes is shown in Figure 37, as the electrical resistance vs gap width. The pre-crack resistance was beyond the measurement capabilities of the instrumentation; consequently, a value of 0.135 Ω was assigned as the starting resistance, based on the geometry of the sample and the resistivity of pure bulk Ag (1.6×10^{-6} Ωcm)[156]. (The 10 µg/cm² SWCNT-MMC maintains electrical connection at the initial fracture, with the resistance increasing only by ~2.5x at a crack width of ~2.8 µm. As the gap widens, the resistance increases minimally by ~3.4x (0.46 Ω) before failing electrically at a total gap width of ~5.5 µm. This is representative of the successful SWCNT-MMC samples, which generally maintained their electrical performance for gap widths up to ~6 µm. The proof of concept images of SWCNTs bridging gaps of ~3 µm (Figure 23) are thus consistent with the electrical test data. The notable exception was one of the grid fingers on the 2 µg/cm². For this sample the resistance increased by ~4.5x at the initial crack length of 5.57 µm. After the initial crack, the sample maintained fairly consistent electrical performance, increasing by another 4x (2.91 Ω) up to a gap width of ~11 µm. The fact that this sample outperforms all other samples is consistent with the free-standing film mechanical data, in which the highest toughness was observed in the 2 µg/cm² samples. Based on the trends in mechanical data, it is proposed that at the initial crack, the small increase in resistance is due to partial or complete failure of the Ag. The change in resistance also depends on the length of the initial crack, with larger changes in resistance observed for larger initial crack length. As the gap in the electrode increases, the resistance increases due to fewer SWCNTs available to bridge the gaps. The resistance remains in the mΩ range for all samples under 6 µm, and in the case of the best performing sample, the
resistance remains in the single Ω range even at gaps of over 10 μm. Thus the SWCNTs may be capable of maintaining adequate performance in the event of solar cell fractures, provided that the fractures are not larger than 5 – 10 μm.

Figure 37. Results of RACK electrical testing showing the resistance versus gap width for MMCs with 2 μg/cm² and 10 μg/cm² SWCNT layer weight loadings.

Although the initial electrical, SEM, and mechanical results show an improvement for SWCNT-MMCs as compared to Ag-only electrodes, the incorporation of MWCNTs into the MMCs may extend the crack bridging capabilities of the structures, as MWCNTs are typically much longer than SWCNTs. Figure 38a and b show MWCNT films of 5 μg/cm² and 20 μg/cm², respectively. The MWCNTs have much larger diameters than the SWCNTs, which changes how the MWCNTs pack together into a film. Thus the
MWCNT films have much more void space and height than SWCNT films with equivalent areal densities, as confirmed by profilometry and SEM measurements. SEM analysis reveals that successive depositions of Ag top-layer up to 4 µm is not sufficient to fully encapsulate the MWCNTs, despite filling of the void space in the 5 µg/cm², as shown in Figure 38c and d. This thickness of Ag is approaching the upper limit for solar cell electrode thickness; therefore no additional Ag was deposited.

Figure 38. SEM images of as-deposited MWCNT films with areal densities of (a) 5 µg/cm² and (b) 20 µg/cm², and over-coated with 4 µm of evaporated Ag.

SEM analysis was also performed to assess the ability of the MWCNTs to mechanically bridge gaps caused by substrate fracture. Figure 39 shows a representative
SEM of a MWCNT-MMC, with the MWCNTs bridging a gap of ~15 µm, and other samples exhibited similar bridging, up to 40 µm.

Figure 39. SEM images of a MWCNT-MMC showing MWCNTs bridging a gap in the Ag of ~15 µm.

Despite the inability to fully encapsulate the MWCNTs in Ag, the SEM analysis clearly indicates that MWCNTs can span much larger gaps than the shorter SWCNTs. Thus, MWCNT/SWCNT “hybrid” films were used in fabricating test structures for further RACK electrical testing. Two samples were fabricated with SWCNT/MWCNT ratios of 80%/20% and 20%/80%, by weight, with CNT film areal densities of 5 µg/cm². Although SWCNT-MMCs with 2 µg/cm² SWCNT performed the best in both mechanical and electrical testing, an areal density of 5 µg/cm² was chosen for the SWCNT/MWCNT hybrid MMCs because of the increased void space caused by the large MWCNT diameter, which was previously addressed in the discussion of Figure 38a and b. A
representative RACK electrical data set for each sample is shown in Figure 40. The 80% SWCNT sample exhibits a 2x increase in resistance upon initial fracture of 1.73 µm, while the 20% SWCNT sample exhibits an 11x increase at an initial fracture of 2.22 µm. The 11x increase in resistance is also higher than that observed in Figure 37 for a similar initial fracture, which resulted in only ~2x increase in resistance. This more significant increase in resistance for the 20% SWCNT sample is likely due to the fact that there are less SWCNTs to bridge the initial fracture. As the gaps are widened to ~5 µm, both samples exhibit an increase in resistance by an order of magnitude to between 50 and 70 Ω, which further supports that the SWCNTs are able to maintain reasonable electrical performance when fractures are less than ~6 µm. However, the resistance at this gap extension is larger than the resistance of the pure SWCNT-MMCs at roughly the same gap width (as shown in Figure 37). It is proposed that SWCNTs can still provide electrical pathways, but as they are randomly dispersed and entangled within the MWCNT network, the number of pathways composed purely of SWCNTs decreases. Put another way, the SWCNT network is likely below the percolation threshold for maintaining electrical resistance in the single Ohms. This is also consistent with observations in chapter 1.2.1 that there will be higher resistance at CNT junctions, and this resistance will increase with increasing heterogeneity.

Above a 5 µm gap width, the resistance of each sample increases to the kΩ range at an extension of ~10 µm. Beyond 10 µm gap width, the samples both increase in resistance until electrical failure at an extension of ~28.5 µm. All other grid fingers for both samples also consistently failed electrically between 20 and 30 µm. Despite the similar performance, the 80% SWCNT sample does experience more significant
increases in resistance as the gap widens. This is likely due to the fact that the less conductive MWCNTs are providing a majority of the electrical and mechanical bridging above 10 µm gap widths, but that there are much fewer of them to contribute to the conduction than in the 20% SWCNT sample. Overall the results show that the addition of MWCNTs provides mechanical and electrical connection at much longer gap widths than the previous tests with SWCNTs-only. However, from an application perspective, a resistance of kΩ is not appropriate for a solar cell electrode, and therefore strategies to increase the MWCNT loading or conductivity would be necessary to facilitate the desired performance for larger gaps.

Figure 40. Electrical resistance versus total gap width for SW/MW-MMC electrodes with SWCNT/MWCNT weight ratios of 20%/80% and 80%/20%.
6.5 Conclusions

A fabrication process has been developed to create layered MMCs utilizing SWCNTs, MWCNTs, or combinations thereof. The techniques are all compatible with standard microelectronic engineering processes. SEM analysis of fractures and the grain structure were used to understand the effects of CNT layer thickness on the overcoated Ag, and to observe CNTs mechanically bridging gaps in Ag upon fracture, thus demonstrating the utility of these advanced materials. An innovative method was used to fabricate free-standing Ag-SWCNT MMC thin films and the resulting films were characterized to understand their response to applied tensile stress. Improvements in mechanical properties of the MMCs occurred as the SWCNT layer thickness was increased to 20 nm, exhibiting a 2.5x increase in toughness. Higher SWCNT loadings led to degradation in performance. SEM analysis and mechanical results suggest that the MMCs transition from a reinforced structure to discrete layers between 20 nm and 50 nm SWCNT layer thicknesses. These SWCNT layer thicknesses correspond to SWCNT areal densities of 2 µg/cm² and 5 µg/cm², respectively. The highest performing MMC with 20 nm SWCNT layer corresponds to ~0.5 vol. % SWCNTs in the composite. The free-standing film mechanical testing provides the important first step toward understanding the optimum SWCNT loading in the MMCs and provides a fundamental basis for which further studies can expand and develop additional improvements for advanced MMC electrodes. The results of electrical testing and SEM analysis of the MMCs under stress suggest that SWCNT-MMC electrodes give an advantage over Ag-only. The SWCNTs are limited in crack-bridging capabilities, but are able to maintain electrical performance up to ~6 µm gap widths due to SWCNT length. Incorporation of much longer MWCNTs
into the SWCNT-MMCs results in ~4× to 5× increase in crack-bridging capabilities, which may be useful if it is found that some solar cell or flexible electronics applications suffer from gaps larger than 6 μm. This work represents a significant step toward realizing more robust electrodes. Ongoing work is being conducted to apply the fabrication processes discussed in this chapter to 29.5% ZTJ cells from SolAero, and also for solar cells grown epitaxially at RIT.
7 Dissertation Conclusions

This work has examined several different facets of metal interactions with carbon nanotube networks, which are all related to aspects of space exploration, including harsh radiation environments and their effects on CNT-metal interactions and interfaces, as well as CNT-metal structures for use as advanced electrodes for space applications. The primary contributions of the dissertation were spatial defect profiling of ion irradiated SWCNTs, modification of SWCNT-Ag electrical interfaces using ion irradiation, and development of carbon nanotube metal matrix composites.

Regarding spatial defect profiling, methods were developed to utilize electrochemical interactions between Au salt solutions and ion irradiated SWCNTs to identify the spatial distribution of defects at the surface of the SWCNT network. This work established a direct correlation between the areal density of deposited Au-nanoparticles and the relative increase in structural damage in the materials. In addition to providing a means to probe ion-generated defects in SWCNTs, the technique can also be used as a method to controllably deposit a desired number of metal nanoparticles onto SWCNTs for other applications. For instance, it may be possible to utilize the deposited Au-NPs as a seed layer for over-coating of other metals, wherein the Au-NPs act as anchor sites to improve adhesion or binding between the SWCNTs and a given metal. This may be particularly useful in the fabrication of MMCs, where delamination of the Ag layers from the SWCNTs was sometimes observed. If the technique were extended to MMCs, an important consideration would be that the level of damage introduced in the SWCNTs would not impede the electrical bridging capabilities of the SWCNTs in the
event of fracture. Thus, the proper relationship would need to be established to maximize the Au-NP deposition while minimizing electrical degradation of the SWCNTs.

Concerning harsh radiation environments, it was shown that ion irradiation can significantly impact the electrical properties of the CNT-metal interface if the ion kinetics and the metal contact thicknesses allow for penetration of the ions through metal contacts deposited onto SWCNTs. This represents the first known study of its kind. It was observed that contact resistance of ion irradiated Ag-SWCNT structures increased by 4x while the transfer length and specific contact resistance decreased by 15x and 4x, respectively. These observations indicate that the Ag-SWCNT electrical transport has actually been improved, while transport through the bulk SWCNTs has been degraded, and this degradation outweighs any enhancement of the Ag-SWCNT electrical interface. Further analysis by computer simulations suggests that the enhancement of the Ag-SWCNT interface is likely the result of creating an Ag/SWCNT composite layer just beneath the contacts that is ~9% Ag/91% C. Overall the work suggests that exposure to lower ion fluences or utilizing very thin SWCNT films may result in improved $R_C$ values as well. Ultimately this work shows that ion irradiation could be leveraged as a tool for modifying the electrical properties of the Ag-SWCNT interface, and with the aid of SRIM and TRIM simulations could be extended to other CNT-metal systems/ion species to generate similar effects. From a practical perspective, the research provides a method for understanding the proper thickness of metal contacts needed for shielding metal-CNT interfaces in scaled CNT-based devices.
In order to address issues related to mechanical and vibrational stresses that are commonly experienced in mounting, launch, and deployment of spacecraft, metal matrix composite electrodes were fabricated with CNTs as reinforcement. The MMCs were rigorously characterized in terms of microstructure, mechanical, and electrical performance under stress. In the process, an innovative method was developed to release the MMCs as free-standing films and assess their mechanical properties through traditional tensile testing. The results were used to understand the appropriate CNT layer thickness needed to achieve reinforcement, and demonstrated improvements in the mechanical properties (i.e. toughness, strain-to-failure) as compared to pure Ag electrodes. Another contribution of the work was the demonstration that both MWCNTs and SWCNTs can mechanically and electrically bridge gaps in the Ag caused by propagation of fractures from the substrate. The development of more robust CNT-MMC electrodes through standard microelectronic engineering processes has significant impact for space solar cells, which often experience reduced power output caused by fractures in the contact metallization. These advanced electrode structures additionally have potential to be used for electrodes in flexible electronics, which would benefit from improved mechanical performance.
Appendix A

This appendix contains figures relating to the discussion in the Spatial Defect Profiling section (Chapter 4). These figures originally served as supplemental information for the manuscript published in Journal of Physical Chemistry C[93] and are hyperlinked as cross-references to the main text for the ease of the reader.
Figure A.1: Raman data was collected at 633 nm laser excitation. Raman spectra for each purified and (150 keV 11B+)-irradiated SWCNT paper (a) before and (b) after exposure to 0.01M KAuBr4(aq) are plotted. Each spectrum was normalized to the G-band peak maximum for the pre-irradiated SWCNTs under the same KAuBr4(aq) exposure conditions. The (c) D/G and (d) D/G' peak ratio values for SWCNT papers before (□) and after (◊) exposure to 0.01M KAuBr4(aq) are plotted versus fluence.
Figure A.2: SEM images at 50,000× magnification for purified SWCNT papers exposed to 0.01M KAuBr4(aq) for (a) 30 seconds, (b) 3 minutes, and (c) 10 minutes.
Figure A.3: Histograms of Au-NP radii nucleated on purified SWCNTs irradiated to (a) $1 \times 10^{13}$ (11B+)/cm$^2$, (b) $1 \times 10^{14}$ (11B+)/cm$^2$, (c) $5 \times 10^{14}$ (11B+)/cm$^2$, and (d) $1 \times 10^{15}$ (11B+)/cm$^2$ and exposed to 0.01M KAuBr4(aq) for 30 seconds. The inset in each histogram shows the corresponding cumulative distribution plot, in which the dashed lines represent a weighted trend line through each data set for visual clarity.
Figure A.4: Histograms of center-to-center Au-NP spacings measured along SWCNT bundles for purified SWCNT papers irradiated at (a) $1 \times 10^{14}$ (11B+)/cm$^2$, (b) $5 \times 10^{14}$ (11B+)/cm$^2$, and (c) $1 \times 10^{15}$ (11B+)/cm$^2$ and exposed to 0.01M KAuBr$_4$(aq) for 30 seconds.
References


