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Carbon Nanotube Defects and Carbon Nanotube Composites

DISSERTATION

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in Physics

by

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ABSTRACT OF THE DISSERTATION

Carbon Nanotube Defects and Carbon Nanotube Composites

By

Deng Pan

Doctor of Philosophy in Physics

University of California, Irvine, 2014

Professor Philip G. Collins, Chair

A single-walled carbon nanotube (SWCNT) is a one-dimensional (1D) conductor that has been proposed as an ideal element for novel, nanoscale electronics. This dissertation studies the properties of individual SWCNTs in the near-pristine limit where the SWCNT conductor contains one or more defects. The presence of defects significantly modifies the electronic and chemical properties of a SWCNT, with positive and negative impacts on different potential applications. This dissertation completed three different types of experiments to explore these modified properties.

In the first section, SWCNTs with defects were studied during high temperature annealing. Annealing rearranged and diminished the scattering from defects, even to a point where pristine SWCNT conductances were recovered. In the limit of single defects on single SWCNTs, the annealing of one defect was resolved in real time by using electrical conductance as the probe. The work proved that conductance in 1D is sufficiently sensitive to see the annealing of one defect.

The resistance associated with single SWCNT defect was also studied as a function of bias and temperature at low temperature. A single point defect surrounded on either side by quasi-ballistic, semi-metallic SWCNT was a nearly ideal system for understanding the influence of functional groups on 1D conductors and comparing experiment to theory. Here,
transport and local Kelvin Probe Force Microscopy (KPFM) independently demonstrated high-resistance depletion regions over 2.0 m wide surrounding a point defect in a SWCNT. A defect assisted tunneling through this depletion region via a modified, 1D version of Poole-Frenkel conduction. Given the breadth of theory dedicated to the possible effects of disorder in 1D systems, it was surprising to find that a Poole-Frenkel model could successfully describe defect scattering in SWCNTs.

Finally, the third experiment investigated SWCNTs that had been non-covalently modified with a thin coating of Cu. Bulk CNT/Cu composites have been reported to have surprisingly high conductance and ampacity. Consequently, CNT/Cu composites are a novel conductor with many potential applications. Here, individual SWCNTs were coated with Cu by electrodeposition for electrical studies. Due to SWCNT’s hydrophobic and inert surface, achieving conformal Cu coatings was very difficult, but successful results were obtained using both aqueous and non-aqueous Cu electrolytes. The thinnest conformal Cu coatings (40nm) were obtained from electrodeposition in non-aqueous Cu electrolyte. Electrical measurement of Cu-coated SWCNTs revealed a similar temperature dependent to the bulk composite, indicating that the SWCNT plays an essential role in the composite conductance’s temperature dependence. However, unlike the preliminary reports, Cu films at these thicknesses could only achieve a fraction of the conductivity of bulk Cu. Therefore, the research was unable to fully test the mechanisms of the improvements reported for bulk CNT/Cu composites.
Chapter 1

Introduction

In the 25 years since their discovery, carbon nanotubes (CNTs) have evolved into one of the most intensively studied materials. CNTs are hollow, cylindrical tubes of graphitic carbon, and a single-walled carbon nanotube (SWCNT) is a single layer of graphitic carbon rolled into a tube with a diameter of 1 to 2 nm. These quasi-molecular systems can be grown cm long, yielding a material with an unprecedented length/diameter aspect ratio exceeding $10^7$.\[1\]

In addition to this unusual geometry, CNTs have various physical properties - electronic, optical, mechanical, and chemical - that make them a unique building block for a wide range of potential applications including fabrics, filters, electronics, and batteries. Composites of CNT with polymers are being investigated for various applications including bulletproof vests that take advantage of CNT’s strength, photovoltaic cells taking advantage of CNT’s absorption in the visible and near-infrared, and flexible thin-film displays based on CNTs as flexible electrical conductors.\[2\]

A particularly promising application of CNT electronic devices is as ultrasensitive chemical sensors. Due to their size and unique electrical properties, CNTs are sensitive to their surrounding environment. Electronic devices made out of individual CNTs have been reported
to be practical sensors for a wide range of analytes. The first such reports, published in 2000, showed that the conductance of individual CNTs changed in response to air exposure and to more aggressive gases like NH$_3$ and NO$_2$.\cite{3} Since then, most experimental efforts in CNT sensing have focused on solving the primary difficulties associated with taking advantage of this sensitivity. For example, CNT sensors are extremely sensitive but not very selective, and cross-sensitivity of CNT conductance to moisture, oxygen, and other contaminants makes prototype sensors noisy and unpredictable from one device to another.

The most common approach to improving selectivity has been through functionalization of CNT devices with other sensitizing molecules. This functionalization can be non-covalent or covalent. For example, a permselective membrane can be non-covalently deposited over a CNT sensor. In this case, the coating limits the analytes to which the CNT is exposed without significantly changing the underlying response of the CNT. On the other hand, covalent functionalization methods attach molecules to the CNT sidewall. In the covalent case, the sensor response of the composite molecule-CNT system can be very different from that of the pristine CNT. In general, the electrical performance of the CNT device is also degraded by covalent functionalization, leading to a practical tradeoff in signal-to-noise between chemical selectivity and conductivity.

The Collins research group at UCI has investigated the chemical sensing properties of CNTs for many years. A recent project investigated SWCNTs having single covalent defects, and their sensitivity to H$_2$ gas when those defects were decorated by Pd nanoparticles.\cite{4} This research showed that defective SWCNTs were more sensitive to H$_2$ than pristine SWCNTs, and that Pd at a defect site further amplified the defect’s sensitivity. In other work, enzyme molecules were non-covalently tethered to SWCNT devices, converting the devices into sensors for probing the dynamic motions of a single enzyme molecule.\cite{5} In both the covalent and non-covalent cases, additional research is needed to understand the CNT conductivity and the mechanisms that can cause to chemical sensitivity. Covalent modifications, in
particular, produce a hybrid molecule-CNT conductor that are not understood theoretically.

This dissertation is focused on the electronic properties of modified CNT conductors. In all of the research, single SWCNTs were studied in field-effect transistor device configurations. The electrical properties of a SWCNT were measured before and after chemical modifications, so that the consequences of the modifications could be clearly determined. Furthermore, covalent modifications were often limited to single-molecule changes to a SWCNT. In the dilute limit of a single molecular attachment, the change in electronic properties can be unambiguously identified with the addition. When the attachment is chemically simple, such as the covalent addition of an alcohol group (-OH) or an ether (-O-), the CNT is considered to have a point defect. Understanding the electronic properties of these point defects underlies experimental control over CNT sensors. The topic is also critical for the future of CNT transistors and other digital electronics, since it could lead to new strategies for limiting the negative consequences of defects.

These aspects of the research methodology are unique in the field of CNT research. Most of the literature on CNT sensors has used films of CNTs, where ensemble averaging eliminates the possibility of understanding how different CNTs contribute to the overall response. CNTs can be either metallic or semiconducting, with a bandstructure that is sensitive to chirality, and the theoretical literature predicts that different chiralities should exhibit different responses to adsorbed molecules and to covalent modifications. Only a small subset of CNT research investigates individual CNTs to determine whether this prediction is true. And while films have been studied with varying degrees of disorder and heterogeneity, virtually no research has been accomplished in the limit of individual point defects. Studying point defects, and particularly studying the same CNT before and after introducing a point defect, is not represented in any of the published literature except by past and ongoing work of the Collins group.

The remainder of this dissertation is organized into three chapters corresponding to three
independent investigations. First, Chapter 2 discusses experiments on the thermal annealing of damaged SWCNTs. The conductance of SWCNTs with defects was monitored \textit{in situ} during annealing in an attempt to watch changes in conductance occurring during the thermal reduction of individual defects. Next, Chapter 3 describes the electrical resistance associated with single point defects. Using a combination of two-terminal transport and Kelvin Probe Force Microscopy, the resistance associated with a single defect in a SWCNTs was measured and fit to a model of one-dimensional Poole-Frenkel emission. Finally, Chapter 4 describes experiments to non-covalently coat SWCNTs with Cu thin films. These experiments were motivated by a desire to achieve the conductivity of Cu in a composite material having lower weight and higher ampacity than pure Cu.
Chapter 2

Temperature programmed desorption of SWCNT defects

2.1 Defects and contamination in SWCNTs

No material can be completely absent of defects or other kinds of disorder. Even when a low density of defects is present, however, most electronic circuits still perform perfectly. Typical conductors can electrostatically screen their defect sites and maintain plenty of unaffected conduction channels. However, when the dimension of a conductor is reduced, the effects of defects can become more critical. Research has revealed that in one-dimensional (1D) conductors, the presence of defects can drastically influence electronic properties. In 1D, charge carriers are confined to a single trajectory and cannot avoid a scattering center or scatter into nearby momentum states.

A SWCNT is a nearly ideal 1D conductor. Its conductance can be significantly degraded by individual defects. Therefore, the practicality of using SWCNTs as transistors or interconnects in electronic applications depends on developing strategies to lower SWCNT defect
density or to limit the types of defects with the most negative consequences.

There are many kinds of defects and disorders in SWCNTs, including intrinsic defects, defects introduced by processing, and disorder in the surrounding environment. Intrinsic defects grow during the process of SWCNT synthesis. These defects include vacancies, interstitials, bond rotations and non-hexagonal rings. The equilibrium concentration of vacancies in SWCNTs can be as low as $10^{-15}$ (1 defect per $10^{15}$ carbon atoms) in SWCNTs synthesized by chemical vapor deposition (CVD) at 1200 K. For comparison, SWCNTs synthesized in a 3000 K plasma have a defect density of $\sim10^{-6}$. [6] With a typical channel length of 2 um, the SWCNT devices used here incorporated approximately $10^6$ carbon atoms. Thus, the CVD process was able to produce an abundance of SWCNT devices having no intrinsic defects. Extrinsic defects are far more common than intrinsic ones. These include environmental disorder such as weakly bound adsorbates and covalent oxidation. These types of disorder are often introduced by processing, purification, chemical oxidation, and other functionalization, and they substantially degrade SWCNT properties.

A standard method of investigating defects is thermogravimetric analysis (TGA). In modern TGA experiments, a sample is heated in either air or vacuum and mass spectrometry is used to measure desorbed gases and gaseous reaction products. Graphite and similar graphitic materials have very low vapor pressures and sublime above 2400 °C, so gases evolved at lower temperatures can be attributed to contaminants and defects. By measuring the partial pressure of desorbed gases such as H$_2$O, O$_2$, CO and CO$_2$, TGA determines the temperatures at which oxide defects and vacancies anneal. Early research with CNTs used the TGA method extensively to probe the purity of bulk material and investigate the effects of vacuum annealing on physical properties. More recently, the desire to reduce graphene oxide into graphene has led to a resurgence of TGA experiments.[7, 8, 9, 10][11] In both cases, TGA has been critical for understanding the appropriate temperature ranges for annealing, the practical temperature limits of the material, and the chemical processes that lead to improvements of
physical properties.

The primary problem with TGA is that it cannot be used to evaluate nanoscale quantities. TGA analysis typically requires mg samples, and such quantities are rarely homogeneous in CNT or graphene research. Consequently, TGA data represents ensembles of defects. TGA is not able to distinguish different species of oxide defects that have similar desorption profiles or different thermal reduction kinetics. In addition, TGA cannot quantitatively assay defect concentrations in low limits. Instead, TGA works best when the quantity of defects is >0.1%, which is many orders of magnitude larger than the concentrations desired for electronic devices.

This chapter describes an effort to avoid ensemble averaging and observe the thermal annealing of single point defects. The premise of the experiment was to take advantage of SWCNT sensitivity and “observe” the thermal reduction of individual defects through electrical conductance instead of by mass spectrometry. SWCNT devices were prepared with defects and then measured using two different methods. In the first set of experiments, devices were annealed in a furnace filled with Ar to determine the threshold temperatures at which SWCNTs start to recover their conductance. After determining this range with numerous devices, individual SWCNTs were measured in a special UHV apparatus that allowed in situ conductance measurements. In this second set of experiments, reduction events were resolved in situ, in real time, as each SWCNT was heated.
2.2 Experimental Methods

2.2.1 Creation of defects

In 2007, the Collins research group at UCI reported a conductance-controlled process to create point defects on SWCNT sidewalls without submicrometer lithography or precision mechanical manipulation.[12] The functional groups obtained were single molecular groups covalently attached to the sidewall of SWCNT devices. This project repeated this process to prepare SWCNTs with one or more defect sites.

2.2.1.1 Miniature electrochemical cell

Experiments used a homemade, miniaturized electrochemical cell. The cell was designed for controlling electrochemical reactions on chip surfaces like our SWCNT devices. The cell consisted of a counter electrode (CE), a reference electrode (RE), and a working electrode (WE).

In order to functionalize SWCNTs, a negative potential relative to the SWCNT (as WE) was applied to the CE using a Keithley 2400. An internal PID loop within the Keithley 2400 controlled the output in 4-wire mode. By connecting the sensing terminal of the Keithley 2400 to the RE, the WE was held at the desired potential relative to the RE. In most of the work, platinum was used as a pseudo-reference electrode. Empirical experience suggests that Pt was stable for hours without much fluctuation. But if the solution was changed or the Pt was exposed to air, the potential could drift. The Pt RE was checked against a standard RE, such as an aqueous Ag/AgCl reference.
Ag/AgCl references are typically encased in a small PTFE tube filled with 3M KCl solution that contains a porous ceramic frit at one end to allow voltage measurements in aqueous solutions. By encasing the Ag/AgCl RE in KCl, it is able to provide a stable surrounding for Ag/AgCl wire, including maintaining the surrounding solution’s composition and concentration, so that the RE is stable and reliable. However, compared to a Ag/AgCl reference, the bare Pt RE had a much faster response rate to changes in potential, and this fast response was important for SWCNT modifications. Thus, a Pt pseudo-reference was used for SWCNT experiments, and Ag/AgCl was used as a cross-reference before each experiment.

2.2.1.2 Conductance-controlled electrochemical functionalization

The schematic in Figure 2.2a shows a SWCNT 3-terminal circuit for electrochemical modification. By applying a negative voltage at the CE, negative ions in the electrolyte were driven towards the SWCNT. At low bias, these ions doped the SWCNT. Covalent functionalization occurred when the voltage exceeded a critical doping threshold and functional groups started to attach to the SWCNT sidewall. The attachments occurred by converting carbon atoms in the sp² lattice to an sp³ hybridization. The remarkable sensitivity of conductance to small compositional changes arises from the 1D conductance of SWCNTs, which amplifies the effect that a single sp³-hybridized carbon can have among 10⁶ sp²-hybridized carbons.
Figure 2.2: (a) Schematic of a 3-terminal circuit for functionalizing a SWCNT device. (b) Current through the SWCNT drops to zero because of functional groups attaching

With conductance as an indicator, we were able to control the amount of functional groups by controlling the duration that an oxidizing potential was applied to the SWCNT WE. The CE potential was gradually decreased (and the WE gradually increased, with respect to Pt) until the conductance began dropping. A typical potential was CE = -1.25 V vs. Ag/AgCl for oxidation in sulfuric acid. Oxidation was also sometimes performed in water, as described in previous work. Longer oxidation durations accumulated more functional groups on the SWCNT sidewall. At the end of the desired treatment, the CE was returned to a “neutral” potential, defined here as -0.55 V vs. Ag/AgCl, at which no further chemical modifications occur.

Throughout this chapter, devices were electrochemically oxidized until the moment their conductance dropped to zero. A trigger with a response time of 0.1 to 0.5 s was used to identify this event and set the WE potential to neutral. After oxidation, the devices were not electrochemically reduced, though reduction may have occurred spontaneously when the electrical control was turned off.
In this technique, the first covalent functional group always attaches to a random, unpredictable position along the SWCNT. Once this first group has attached, the defect site becomes much more electrochemically active. All later functional groups tend to attach to neighboring locations rather than nucleating new damage at other points along the SWCNT. This clustering behavior has been confirmed with scanning probe microscopy in previous research.\[12\] In this work, small numbers (i.e. 3 to 5) of adjacent covalent modifications were defined to be one single “defect”. A second defect would be another cluster nucleated at an independent location on the SWCNT.

2.2.2 *Ex situ* annealing in a furnace

Some SWCNT devices were annealed using an air-tight, 6” quartz tube furnace. The furnace system included a gas flow control box and a custom LabVIEW control software that regulated gas flow rates and durations. After introducing oxide defects into SWCNT devices, the devices were loaded into the furnace and the system was flushed with argon gas (4000 sccm) for 8 minutes to remove most of the air. Samples could then be moved from the furnace cold zone into the hot zone (up to 1200 °C) and back without opening the system or exposing samples to air. This process helped protect the SWCNTs from oxidation, though some samples were lost (oxidized to the point of becoming completely insulating) because the Ar flush incompletely removed all reactive O$_2$.

The procedure in this experiment was to anneal each device at a fixed temperature for 10 minutes and then retrieve the sample and remeasure its electrical properties. The same device was annealed and remeasured multiple times, beginning at 100 °C and increasing in 100 °C increments up to 600 °C, and then finally at 900 °C.

The primary electrical characterization was to measure the source-drain current $I$ as a function of the back gate voltage $V_G$. The resulting $I - V_G$ curve determined the highest
conductance value of the SWCNT, which was defined as the on-state conductance $G_{on}$ of the device. The on-state conductance was recorded before functionalization, after functionalization, and after each anneal run. Then, all of the values were compared to determine the effect of annealing and the temperature at which the pristine $G_{on}$ was recovered.

Some of the SWCNTs fully regained their initial $G_{on}$ after the first cycle of annealing at 100 °C. Previous research has indicated that some type of defects can remain attached, even when $G_{on}$ is recovered.\[12\] In order to test for this possibility, the devices were subjected to a second round of electrochemical functionalization. The presence of residual disorder was detected as a smaller threshold for electrochemical re-oxidation. Repeated cycles of annealing and re-functionalization were terminated when the $G_{on}$ could no longer be recovered using a 900 °C treatment, or if a SWCNT became insulating.

### 2.2.3 In situ annealing in ultra high vacuum

After functionalization, other SWCNT devices were annealed in ultra-high vacuum (UHV) using a custom designed rapid thermal annealer (RTA) apparatus. The RTA was built as shown in Figure 2.3. The system consisted of a UHV system, a portable heater with probes to provide electric connection to SWCNT devices, and electrical feedthroughs to provide control and measurement into the UHV system. This RTA could anneal devices in vacuum with four probe configuration without exposure to oxygen or moisture.

Previous work with the RTA measured the conductance of pristine SWCNTs during annealing. Comprehensive experiments compared the effects of annealing on Ti, Pd, and Pt electrodes. The surface chemistry of annealed Pt electrodes, and changes in SWCNT noise during annealing were studied. \[13, 14\]
Figure 2.3: The schematic of UHV Rapid Thermal Annealer
The UHV RTA system consisted of two stainless steel vacuum chambers. Annealing was performed in the main chamber. The other chamber was a load lock that could be opened to atmosphere. The sample could be transferred from the load lock to the main chamber through a gate valve using a magnetic manipulator. There, the sample plugged into high-temperature, electrical feedthroughs that locked into the sample heater. Vacuum was provided by an ion pump, a magnetic-levitation turbo pump (SEIKO SEIKI STP-451C), and a roughing vacuum line to an oil-free, dual-scroll roughing pump on the other end. Typical pressures were 10 to 20 mTorr in the roughing line and as low as $10^{-8}$ Torr in the main chamber.

Sample heating in the RTA was provided by a boron nitride (BN) heater on a portable puck. The BN heater was a 60mm by 39mm rectangular surface shown in Figure 2.4a. This heater was rated for temperature as high as 1500 K, voltages as high as 110 V, and a current of 16 A. The heater was powered by an external power supply controlled by a PID loop in LabVIEW. Both the rate of heating and cooling could be controlled.

SWCNT devices sat on a larger, Ti-coated chip in the center of the BN heater. Four tungsten probes contacted and pressed down on the SWCNT devices as shown in Figure 2.4b. Two adjacent probe were normally placed on the same electrode pads so that the device could be characterized with 4-wire sensing method. The use of a 4-probe configuration to measure the conductance of SWCNT helped to exclude any temperature sensitive resistance other than the SWCNT resistance. The probes were insulated by hollow cylindrical alumina beads and connected to the banana plugs at the back of the puck as shown in Figure 2.4c. Extra alumina beads at the bottom of the tungsten probes insulated the probes from each other. A fifth probe touched down on the Ti film and connected to the back gate of the device. The back gate shifted the SWCNT Fermi level during the experiment.

A thermocouple monitored the surface temperature of the BN heater. The thermocouple was a type K (chromel-alumel) thermocouple rated for a temperature range of 200 to 1500 K.
The thermocouple was electrically insulated by alumina beads and connected to the banana plugs at the back of this portable puck as in Figure 2.4c. The SWCNT temperature was assumed to be the same as the BN temperature measured by this thermocouple.

At the back of this puck, there were a few banana plugs connecting to the tungsten probes, thermocouples and the power line for the BN heater. In the main UHV chamber, these banana plugs gently inserted into sockets connecting to the outside of the chamber. When loaded, the puck locked into place securely. These banana plugs also had alumina beads to insulate them from the puck’s metal body, and these alumina beads were wrapped with alumina ribbon to further protect them from metal evaporation at high temperatures, as shown in Figure 2.4c.
The load lock included an infrared heating lamp to preheat the back side of the sample holder and bake off most of its moisture. After loading each device into the load lock and evacuating, the sample holder was baked up to 100 °C for 30 min to remove excess moisture. The actual surface temperature of the SWCNT probably never exceeded 50 °C and was certainly below the thermal reduction temperature of most SWCNT defects. Thus, we believe there was little chance for thermal reduction or defect desorption reactions to occur during the baking treatment. After baking, the device was loaded into the main chamber for measurement.
2.3 Results for *ex situ* annealing of defects

Figure 2.5a shows the normalized value of $G_{on}$ after each cycle of anneal, relative to the pristine conductance $G_0$. Each SWCNT device was functionalized to the point of being insulating, so the conductance curve begins at $G_{on} = 0$ at 25 °C outside of the chart. After the first anneal at 100 °C, $G_{on}$ recovered to about 2%$G_0$. $G_{on}$ recovered to 80%$G_0$ after annealing at 300 °C, and it fully recovered after the 400 °C cycle.

![Graph](image)

Figure 2.5: (a) Recovery of on-state conductance ($G_{on}/G_0$) for a SWCNT device versus the temperature $T$ of each annealing cycle. (b) $G_{on}/G_0$ versus $T$ of the same SWCNT after a second cycle of electrochemical functionalization

After this first round of functionalization and reduction, the SWCNT device was chemically functionalized again in the same electrolyte. Figure 2.5b shows the ratio $G_{on}/G_0$ for this second cycle. Again, temperatures of 200 to 300 °C recovered the device to almost 80%$G_0$, consistent with the behavior of the first cycle in Figure 2.5a. However, Figure 2.5b shows that upon reaching 400 °C, $G_{on}$ began to drop and the SWCNT became open circuit after the anneal at 600 °C. Further thermal annealing up to 900 °C could not recover any conductance.
Similar results were reproduced using various different samples. In order to compare samples, a thermal reduction temperature was defined to be the lowest temperature at which $G_{on}/G_0$ recovered to at least 1%. Figure 2.6 depicts this thermal reduction temperature for multiple devices. Figure 2.6a shows that for SWCNTs functionalized only once, 5 out of 7 already began to reduce during the 100 °C annealing cycle. This low temperature was consistent with previous research on thermal reduction kinetics of graphene oxide, which started at 70 °C and peaked at 150 °C. [11] While most of the samples began reducing at relatively low temperatures, only 1 of the 7 recovered to $G_{on}/G_0 > 95\%$. Two other devices recovered to 30%$G_0$, and the rest regained < 20%$G_0$. Incomplete recovery, even after annealing at 900 °C, indicates residual damage to the SWCNT. In fact, theoretical calculations suggest that 900 °C should not be sufficient to remove the most stable types of functional groups.

Figure 2.6b shows the thermal reduction temperature for SWCNTs after two functionalization cycles. In their second cycle, all 6 insulating SWCNTs recovered some degree of conductance. However, the temperature for recovery was higher. 4 out of the 6 devices recovered at 200 °C, and 2 recovered at 300 °C. All of the devices also showed an accumulation of degradation. The device that had almost fully recovered reached a maximum $G = 30\%G_0$, but half of the devices only recovered to 1-5%$G_0$. Furthermore, none of the 6 devices survived an anneal at 900 °C for a third cycle of functionalization. 4 SWCNTs became insulating after a 600 °C anneal, and all of the SWCNTs were insulating after the anneal at 900 °C.
In this experiment, the initial full recovery typically required annealing up to 400 °C. This high temperature probably indicated extensive chemical functionalization. In other words, many chemical groups were probably attached to the SWCNT sidewall, perhaps in more than one cluster of covalent adducts. At each temperature from 100 up to 400 °C, these adducts may have been rearranging on the SWCNT surface or chemically reducing into alternate chemical groups that were energetically more favorable. The conductance recovered to a different extent at each temperature because different reactions had different activation energies.

Based on theoretical calculations, even 900 °C should not be sufficient to remove the most stable types of functional groups. Thus, $G_{on}$ may be an insufficient indicator of returning a SWCNT to its “pristine” state. In fact, when $G_{on}$ had fully recovered at 400 °C, the full $I-V_G$ curve was usually observed to have a different threshold and shape than the pristine case. These modest differences suggest that some functional groups remained attached to
the SWCNT after the first cycle of functionalization and annealing.

This conclusion helps to explain why the second cycle of electrochemical functionalization led to the dramatic failures summarized in Figure 2.6b. The second cycle accumulated more damage around the residual defect site. According to theory, the lowest energy configurations of multiple oxygen adducts is a linear arrangement bridging across multiple parallel C-C bonds. [16] This linear arrangement concentrates stress and fractures the carbon lattice. We propose that the second cycle of functionalization, which was initiated from an energetically relaxed cluster of oxygen adducts, may have created this type of disruptive sidewall defect. Rather than annealing at high temperature, the linear arrangements fractured the SWCNT and created open circuits.

2.4 Results for in situ annealing of defects

The ex situ furnace measurement provided limited information. The conductance was measured before and after each anneal run, but what happened inside the furnace was unknown. In addition, the data had relatively large temperature increments of 100 °C. More accurate temperature resolution would have required many anneal runs at smaller temperature increments.

In situ measurements in the UHV RTA were designed to provide a more detailed picture of defect annealing. Damaged SWCNTs were loaded into the UHV RTA and then the temperature was ramped up at a constant rate of 0.2 °C/s. For this experiment, full $I - V_G$ curves were not acquired versus temperature, so the on-state conductance $G_{on}$ was not fully determined. Instead, the back gate was held at zero volts and the experiments measured $G(T; V_G = 0)$. $G$ was measured with a 40 kHz bandwidth preamplifier and digitized at 100 kHz, in an effort to capture and time resolve short-lived events.
Figure 2.7 shows an example of an in situ measurement of $G(T)$ from room temperature up to nearly 500 °C/s. $G(T)$ started from zero, which was equal to the post-functionalization value, until the temperature reached 150 °C. Above $T=150$ °C, the conductance increased through a combination of discrete jumps and smooth, continuous changes. The smooth, continuous changes were interpreted as the temperature dependence of the electrodes, the electrode-SWCNT Schottky barriers, and other ensemble, thermally-activated processes. For example, heating can change the Schottky barrier height and remove physisorbates, two processes which can either increase or decrease $G(T)$. Interplay between such processes was believed to cause the gradual increase of $G(T)$ up to 250 °C and the decrease from 250 to 300 °C.

Between 150 and 250 °C, additional discrete jumps in $G(T)$ occurred on top of the more continuous changes. Jumps at 165, 180 and 200 °C appear in Figure 2.7 as spikes in the $G(T)$ graph. Figure 2.8 shows raw, time-resolved data of $G$ for the instants in time surrounding these jumps. Each graph in Figure 2.8 has a duration of 0.5 s, during which the temperature ramped less than 0.1 °C. The graphs illustrate 3 discrete increases that occurred as the SWCNT was heated. At 165 °C, $G$ jumped up by approximately 40 nS, from 8 to 45 nS. At 180 °C, the conductance increased by 50 nS from 40 to 90 nS. At 200 °C, the conductance increased another 50 nS from 80 to 130 nS. All 3 increases were similar in magnitude and they completed in less than 10 s, the instrumental limit of the measurements. Furthermore, the magnitude and duration of these jumps matched the characteristics of typical discrete decreases observed during electrochemical oxidation (for example, Figure 2.2b).
Figure 2.7: $G(T)$ measured \textit{in situ} during annealing for a SWCNT oxidized in sulfuric acid. Temperature was ramped at 0.2 °C/s and data were acquired at 100 kHz.
Figure 2.8: Raw time traces of $G$ showing discrete increases at 3 temperatures: (a) 165 °C, (b) 180 °C and (c) 200 °C.

All of these characteristics were consistent with the thermal annealing of individual, molecular defects. The increases in $G$ mirrored the decreases reported for electrochemical oxidation.\textsuperscript{[12]}
and the very short durations ruled out large-scale or ensemble processes. Furthermore, a
dramatic decrease of noise was observed for T > 250 °C. Figure 2.7 shows that no additional
discrete events occurred after this noise reduction. Noise and fluctuations have proven to
be a reliable indicator of SWCNT defects, so a return of the device to a low-noise state is
highly suggestive of a return to a pristine, defect-free sidewall.

Similar behaviors were observed in other samples. Initial measurements reliably observed
the recovery of G and a combination of discrete increases on top of continuous increases and
decreases. In many devices, the discrete jumps were poorly resolved. Figure 2.8 represents a
best case that followed a gradual optimization of instrument noise and bandwidth. It was an
experimental challenge to resolve small changes in G with 10^-s resolution in an environment
that included large temperature gradients, vacuum pump vibrations, and other electronic
noise.

Figure 2.9a shows an example of G(T) for another SWCNT. This device was electrochemi-
cally functionalized in de-ionized water instead of sulfuric acid and then measured up to 650
°C at a rate of 1 °C/sec. Similar to the previous case, discrete jumps were observed on top
of a continuous increase of G(T) up to 180 °C. From 200 °C up to nearly 450 °C, the average
G(T) was relatively flat but punctuated by many discrete reversals where G increased and
then decreased by a similar amount. A few of these reversals are highlighted in Figure 2.9b.
This reversible switching was very different from the single, irreversible events described for
the previous SWCNT (Figure 2.8). The noise in G may indicate that the thermal annealing
can be much more complicated than expected, perhaps because of bistable rearrangements
of chemical groups on the SWCNT sidewall. Above 450 °C, the SWCNT noise finally di-
minished and G(T) became smooth and monotonic. This device used a semiconducting
SWCNT, so the final slope of G(T) was positive.

Clusters of reversible switching in Figure 2.9b were probably activated by just one defect at
any particular time. It is possible that a particular type of defect gives this behavior, perhaps
one that is specific to oxidation in water. Oxidation in water is believed to add phenolic alcohols (-OH) to the SWCNT sidewall, whereas oxidation in sulfuric acid is believed to add ether or epoxide (-O-) adducts.[12] This experiment reveals the possibility that each type of chemical defect could have a unique behavior upon heating, but many repeated tests would be necessary to prove this hypothesis.
Figure 2.9: *In situ* $G(T)$ for a SWCNT oxidized in water. (a) The entire record of $G(T)$, heating up from room temperature through a very noisy state, and then cooling back down in a quiet, higher conductance state. (b) A 10 °C portion of the heating curve, at a magnification that resolves reversible jumps of a two-level system. Temperature was ramped at ±1 °C/s and data were acquired at 100 kHz.
2.5 Conclusions and future work

This work observed the annealing of single SWCNT device, both \textit{ex situ} and \textit{in situ}. The recovery of SWCNT conductance $G$ was clearly resolved in both types of experiments, with initial recovery at 100 °C and full recovery below 400 °C. In addition, the research resolved individual reduction events in real time as single point defects annealed. At low temperatures, these events may have been rearrangements into more stable defect configurations. At the higher temperatures, the final rearrangements brought the conductance levels back to the levels of a pristine SWCNT. Subsequent experiments, however, indicated that residual damage remained on the SWCNT, even after processing at 900 °C and even when this damage had only subtle effects on $G$.

The results here were in agreement with previous, ensemble experiments on bulk CNTs and other graphitic materials. The key temperature range of 100 ~ 200 °C measured here matched the generic characteristics of defect thermal reduction measured by mass spectroscopy TGA.[11] No previous research, however, has ever resolved defect annealing on single, isolated nanoscale devices. Thus, the results demonstrate the initial hypothesis that conductivity is sensitive enough to resolve defect annealing at the single defect limit.

This experiment annealed devices up to 900 °C. The RTA apparatus was designed to withstand temperatures as high as 1200 °C, but the current generation of SWCNT devices failed at such high temperatures. The failure was due to gate leakage. The gate oxide in our SWCNT device configuration was a 250 nm dielectric layer of SiO$_2$ insulating the Si wafer from the SWCNT and metal electrodes. When SWCNTs were synthesized by CVD, millions of catalyst particles were spread uniformly on the top of SiO$_2$. During the CVD process,
many of these catalyst particles embed into the SiO$_2$. Later, when biases are applied during annealed up to 900 °C, these catalyst particles degrade the SiO$_2$ insulator with conductive channels. This non-reversible process short circuits the source and drain electrodes to the underlying gate, limiting measurements to < 900 °C.

Future work could solve this problem by limiting the catalyst contamination of the surface. The Collins lab has made substantial progress patterning catalysts for CVD SWCNT growth, and can eliminate all catalyst underneath the source and drain electrodes. With this catalyst patterning, the leakage current problem from high temperature annealing could be solved, allowing SWCNT annealing to be studied at still higher temperatures. At 1200 °C, SWCNT lattice structures can truly anneal and many more functional groups can be removed, so it will be interesting to see what electrical consequences are observed at these higher temperatures.
Chapter 3

Poole-Frenkel Emission in defective SWCNTs

3.1 Introduction

The previous chapter explored the functionalization of SWCNTs and the remarkable sensitivity of SWCNTs to defects and contamination. A single defect can dramatically change SWCNT from a ballistic 1D conductor to a highly resistive nanowire.[17, 18, 19, 20] Driven by these dramatic effects, the International Technology Roadmap for Semiconductors[21] calls for a physical model to better address the role of single defect and dopants on this semi-classical 1D device. Unfortunately, this is a topic where theory and experiment have few points of direct comparison. Theory predicts a range of novel phenomena and practical consequences in disordered 1D conductors,[22, 23, 24, 25, 26, 27] whereas experiments are often limited to random contaminants and imperfections of unknown character. The precision placement of individual atoms into conducting structures, either using scanning probe tips [28] or by implantation.[29, 30] has revealed quantum states at cryogenic temperatures, but
these consequences disappear at high temperatures. SWCNTs, on the other hand, exhibit a quantum-mechanical regime extending to room temperature.\cite{31} Unfortunately, SWCNTs are a poor example of precision control: disorders in SWCNTs is ubiquitous, random and varied.\cite{17,18,19,32} Well-characterized systems for studying defect-induced effects have been acknowledged as a challenging gap to address experimentally.\cite{33}

This chapter uses electrochemically modified SWCNT devices to control the quantity and species of oxide defects in a SWCNT. With careful comparison of conductance before and after the defect incorporation, the difference in conductance and its mechanisms can be studied in greater detail.

### 3.2 Controllable Electrochemical modification

This project used the same experimental methods described in the previous chapter to introduce defects to SWCNTs, but with more precisely controlled steps. A bias was applied across the SWCNT device, so that the current $I_D(t)$ through a SWCNT was a real-time indicator of covalent modifications during the dilute electrochemical oxidation of a SWCNT. In the last chapter, an oxidative potential was held on the CE until the current $I_D(t)$ dropped to zero, and the CE was triggered to a neutral potential manually. Manual control led to less control over the number of defects incorporated and the accumulation of numerous defects. For example, Figure 2.2b shows that 3 different drops in $I_D(t)$, indicating the production of at least three different defects before $I_D(t)$ dropped to zero. Because hundreds of milliseconds elapsed between $I_D(t)$ dropping to zero and the CE being turned off, even more defects may have been incorporated. The exact defect quantity was not a critical parameter in the previous chapter. In fact, multiple defects allowed the observation of multiple thermal reduction events from a single SWCNT.
This chapter, on the other hand, aims to characterize the resistance of a single defect. Achieving this level of control required modification. Instead of triggering the oxidative potential to neutral potential when the current $I_D(t)$ drops to zero, we trigger it when the current $I_D(t)$ drops by 20%, and the response time is narrowed down to 30 ms. Conductance decrease by 20% is defined as the threshold to minimize the quantity of defects incorporated but not to triggered by fluctuations in $I_D(t)$ that occur during functionalization. These fluctuations are partly due to the 1/f noise of the SWCNT and partly due to ionic adsorption events on the SWCNT. Thresholds less than 20% caused too many false positives from such events.

Figure 3.1 shows a typical $I_D(t)$ trace in which a device increased resistance from 430 to 600 kΩ. Unlike the functionalization in the previous chapter, this more controlled functionalization normally had only 1 discrete drop in conductance.

![Figure 3.1: Example drop in $I_D(t)$ used to identify point-defect incorporation by electrochemical oxidation.](image)

Figure 3.1: Example drop in $I_D(t)$ used to identify point-defect incorporation by electrochemical oxidation.
3.3 Experimental Apparatus

To comprehensively understand the effect of oxide defects to SWCNT conductance, a high-vacuum \((10^{-6} \text{ Torr})\), variable-temperature probe station and a high-vacuum \((10^{-8} \text{ Torr})\) and cryogenic atomic force microscope (AFM; JEOL JSPM 5200) was used to acquire transport data and surface maps of local properties.

3.3.1 Desert Probe Station

After electrochemical functionalization, transport measurements were performed on the SWCNT device inside a cryogenic vacuum system. This system is a TTP4 manipulated-probe station manufactured by Desert Cryogenics, a division of Lakeshore Cryotronics, Inc. It can be used for non-destructive electrical testing of devices on full and partial wafers up to 2 inches in diameter. It consists with a turbo vacuum system, cryogenic system, probing system and an optical system.

The high vacuum is provided by a turbo pump (Edwards EXT70H). The turbo pump can provide final low pressure of \(10^{-9} \text{ Torr}\). However because of the cryogenic chamber that Desert Cryogenics designed, the pressure inside this vacuum chamber cannot go that low, but can be as low as 1 Torr in room temperature. Chamber pressure is measured with a BOC Edwards wide range gauge. The turbo pump is backed by a scroll pump which provides vacuum as low as 10-20 mTorr.

The sample holder is thermally and electrically isolated from the rest of the chamber. The holder can be heated up to 450K via a built-in heating resistor controlled by a LakeShore 331 temperature controller. With cryogenic cooling and a temperature controller adjusting the heating power with a PID feedback loop, the sample’s temperature can be regulated precisely.
There is one thermocouple attached to the sample holder to measure the sample holder’s temperature. One of the probe arms has an embedded temperature sensor which can provide a temperature reading of the probing arm. The sign of the sample sitting in an temperature equilibrium condition is that the temperature sensor on the sample stage and the temperature sensor inside the probing arm are within 10K difference. And the temperature reading of the sample holder thermocouple is considered to equal the sample temperature.

A transfer line carries liquid helium or nitrogen from an external dewar to the probe station reservoir. The reservoir is separated from the sample by an additional stage of temperature control. When left unused, direct contact between the components ensures that the sample temperature can be as low as the cryogenic liquid (e.g. either 4.2 K with LHe or 77 K for LN$_2$). Cryogen is routed from the dewar to the refrigerator by a transfer line. This transfer line is designed by Desert Cryogenics specifically for this probe station. One end of the transfer line is the supply side leg which inserts into the dewar and incorporates a foot valve. This valve is used to regulate the flow through the transfer line. The other end is target side leg which is sealed and inserts inside the probe station and all the way into the refrigerator without waste of the cryogen. Between the transfer line legs is a flexible section that is approximately 1750 mm long. This allows the transfer line to be manipulated into the the probe station once the other end is fixed in the Dewar.

There are 4 probe arms with bellows built in with this system to manipulate the probe tips inside the chamber. The bellows provide structural support around the probe arms when the system is under vacuum. The flexible stainless steel bellows allow manipulation of the probes while maintaining the system’s vacuum. Four individual probes of each arm are available to contact multiple devices simultaneously. The original probes of Desert Probe Station are ZN50R DC/RF probes, with tips made of BeCu. The BeCu probe tips are soft and vulnerable to be bent when been approached to the sample surface. Harder probe tips (Micromanipulator 7A) are tailored and soldered onto ZN50R probe blades to replace the
soft tips.

Here in this experiment, only 2 probes were utilized for source-drain conductance measurement, using a Keithley 2400 SourceMeter and Keithley 428 Current Amplifier. Another probe was probed down to the sample holder and connected to an analog out channel on the DAQ board to provide back gate bias for the sample.

3.3.2 JOEL Atomic Force Microscope

This system is consisted of a JEOL AFM and electronic controls. JOEL AFM has built-in turbo pump that can provide a low pressure for the system as low as $10^{-8}$ Torr. The turbo pump shares the same roughing pump line with Desert Probe Station. Sample can be cooled down by copper foils connecting to Dewar filled with LN$_2$, and thin-film resistor samples determined the operating surface temperature to be 185K.

All commands originated from the computer with custom LabVIEW program, destined for either the National Instruments NI-6289 DAQ card, or the AFM controller. The DAQ card controlled the output of source, drain and back gate biases ($V_S$, $V_D$ and $V_G$, respectively) and measurement of the source-drain current $I_D$, as well as the AFM tip position. The AFM controller is responsible for all of the tasks that are required to operate an AFM.

The system is fully equipped for topographic AFM, Kelvin Probe Force Microscopy (KPFM), Scanning Gate Microscopy (SGM), Scanning Gate Spectroscopy (SGS), and Scanning Tunneling Microscopy (STM). SGM is used to map out where a device’s gate dependence is spatially located. [34, 35]When the AFM tip is biased relative to the device, it produces an electric field which only gates a small portion of the device. By using software to correlate device with AFM tip position, an image is generated which shows the spatial location of gate sensitivity. KPFM is utilized to measure the surface potential of SWCNT device. By corre-
lating with AFM tip position, an image is generated which maps out the surface potential of SWCNT device.

Conventional silicon cantilevers (MicroMasch ULTRASHARP NSC15) coated with a 10 nm Pt film were used with an AC modulation of 500 mV at 1 kHz. Surface potential and topography were measured simultaneously using a frequency demodulation and Kelvin force feedback scheme that is typical for KPFM. Specifically, shifts in the cantilever frequency were demodulated by a phased locked loop, tracked using an external lock-in amplifier (Stanford Research Systems SRS 830), and then nulled by a feedback loop that controlled the Kelvin probe potential $\Phi_{KP}$. The FM mode KPFM measurement details and other technical details have been described previously.

3.4 Transport measurements

The SWCNTs with resistance lower than 1MΩ, which were labeled as “clean” devices, were selected for this experiment, because they had low room-temperature inelastic mean free paths and low contact resistances. If any defect incorporated, the oxidized defect sites can be the only inelastic scattering site that sufficiently disruptive to SWCNT conductance at room temperature.

For SWCNTs fabricated from CVD, 1/3 of them are metallic SWCNTs. For ideal metallic SWCNT device, the resistance is independent of back gate bias. However in reality, some of them have minor gate-dependence, which means that there might be some defects or surface contamination on the SWCNT. Previous research demonstrated that the scattering from oxide defects is also gate-dependence.[12] In order to save the effort of distinguishing the gate dependence from previous contamination or defects and the gate-dependence from oxide defects, the SWCNTs that have the least resistance gate-dependence was chosen for
this research.

Because of the controllable electrochemical functionalization, the amount of defects and the effect of scattering from the oxide defect site was much less when comparing to last chapter. The added resistance was comparable to the channel resistance and contact resistance in a pristine SWCNT device. In order to understand the mechanism of transport through the defect site, any resistance other than the newly added resistance from defect incorporation should be eliminated. So it is important to record the transport data both before and after defect incorporation.

A pristine SWCNT device without any prior functionalization was placed in to the probe station and then the chamber pressure is pumped down. After a few hours until the pressure was stabilized, two-terminal measurements of $I_D(V_D, V_G; T)$ was acquired over a wide range of source-drain voltage ($V_D$), back gate bias ($V_G$) and temperature ($T$). The source-drain current $I_D$ was measured first at 300 K, while the back gate bias was swept by a triangle wave from -10 V to +10 V, which is normally called $I - V_G$ curve. For each $I - V_G$ curve measurement, the source-drain voltage $V_D$ was fixed. But in order to get $I_D$’s dependence to $V_D$, $V_D$ was varied from -2.0V to +2.0V. After each $I - V_G$ curve was finished, then $V_D$ was changed to the next value and repeated the measurement of $I - V_G$ curve until the sweep of $V_D$ was finished.

After this 3D data of $I_D(V_D, V_G)$ was measured, LN$_2$ started to pump into the refrigerator underneath the heater. The heater was controlled by a PID loop and set at 230 K. When the thermocouple on the heater and the thermocouple inside one probe arm were different by <10 K, the device was considered to be thermally equilibrium and another set of $I_D(V_D, V_G; T = 230K)$ was measured. The process was repeated at temperature setpoints of 180, 130, 100 and 77 K to explore the temperature dependence with a four-dimensional data set of $I_D(V_D, V_G, T)$. 

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After the initial measurement, the chamber was brought to room temperature and vented with dry N$_2$. The device was removed to a different apparatus for electrochemical functionalization. If the chamber was still cold when exposed to air, moisture condenses on the inside surfaces and extra time would be required to pump down the chamber on the next cycle.

After a careful controllable functionalization, the device was placed back into the chamber of desert probe station and the chamber was pumped down. The 4D data of $I_D(V_D, V_G, T)$ of the device with oxide defect was acquired according to the same procedures as the measurement of pristine SWCNT device.

### 3.5 SGM and KPFM measurement of SWCNT with defects

Right after the two terminal transport measurements, the SWCNT device was taken out of Desert Probe Station and transferred to JEOL AFM for KPFM and other Scanning Probe Microscopy (SPM) measurements. Figure 3.2(a) shows the SGM map overlap with topographic map of SWCNT device. The red spot indicating the region on SWCNT with the highest gate sensitivity was the defect site. Figure 3.2(b) shows that KPFM imaging under back gate bias $V_G = -1V$ resolved a large potential drop at the same location where the defect was incorporated. In comparison, pristine metallic SWCNTs exhibited shallow KPFM potential gradients with large drops at the electrode interfaces [36, 37, 34, 38].
Figure 3.2: (a) SGM image of the localized nature of the new gate dependence; (b) KPFM image illustrating the large potential gradient at the same site.

Higher-resolution KPFM versus $V_D$ and $I_D$ allowed for a detailed investigation of the spatial gradients surrounding a scattering site. Figure 3.3a shows a set of KPFM images acquired with the same device biased from +2.0 V to -2.0 V in 0.5 V increments, from left to right. The data with $V_D = 0 \text{ V}$ is not shown here. Exchanging the role of source and drain produced the most intuitive and directly comparable images of reverse polarity. Images were cropped to highlight the region surrounding the SWCNT defect, and line cuts along the SWCNT channel were extracted for analysis (Figure 3.3b).

Figure 3.3b shows the region from 2.2 to 3.1 m contained a symmetric, high-field potential drop centered around $x=2.65 \text{ m}$, the same locus of SGM sensitivity. At $V_D=1 \text{ V}$, the KPFM potential drop $\Delta V$ surrounding the site was $0.68\pm0.04 \text{ V}$, corresponding to local resistance $\Delta V/I_D = 928 \pm 54 \text{ k}\Omega$ that was two-thirds of the total device resistance. In this manner, KPFM allowed direct measurements of the defect’s resistance, independent of contact resistances and diffusive scattering along the rest of the SWCNT. These other mechanisms determined the inelastic mean free path far from the defect and they have been
previously investigated at low and high bias. [36, 37, 39]

Figure 3.3: (a) Selected portions of KPFM images around a SWCNT defect site at $V_D = +2$ to -2V in 0.5 V steps. (b) KPFM line cuts extracted along the SWCNT, with reverse-bias data plotted as dashed lines.
3.6 Drastic change in conductance after defect incorporation

From the view of transport measurement, Figure 3.4a shows the $I_D(V_D)$ before and after defect incorporation at back gate bias $V_G = -1$ V. Before functionalization, pristine SWCNT device’s $I_D(V_D)$ curve is linear, which indicates an Ohmic conduction. After functionalization, SWCNT device’s conductance is generally lowered because of scattering from the newly added defect. Besides this, compared to the pristine case before modification, the damaged m-SWCNT exhibited a much higher low-bias resistance, a non-Ohmic $I_D(V_D)$. Figure 3.4 illustrates the increases of resistance and gate sensitivity that accompanied the addition of a defect to the SWCNT device, and twice as much gate modulation in $I_D(V_G)$, all in accord with previous reports. [12, 38]
Figure 3.5: $I_D(V_D, V_G=-1 \text{ V}, T=77 \text{ K})$ in Poole-Frenkel scale

Figure 3.5 plots conductance versus square root of $V_D$ over $kT$ on X linear scale both before and after oxide defect incorporation. The pristine SWCNT device has an ohmic, temperature-independent conductance that resulted in nearly-horizontal lines on these axes; the addition of a defect reduced the conductance and induced a non-ohmic bias dependence.

These two-terminal measurements included contact and channel resistance, but careful subtraction of data sets before and after defect incorporation allowed us to define the additional voltage $\Delta V_D$ necessary to obtain the same current $I_D$ at fixed $V_G$ and $T$. This procedure approximates the semi-classical limit of the Landauer-Buttiker formalism, in which each constituent scattering mechanism constitutes a series resistance. So long as point functionalization does not affect the SWCNT’s contact resistance or inelastic mean free path, the addition of one new scattering site introduces an extra voltage drop $\Delta V_D$ for a given $I_D$. A similar distinction between $I_D(V_D, V_G, T)$ and $I_D(\Delta V_D, V_G, T)$ is common in the analysis of radiation damage.[40] The differential data $I_D(\Delta V_D, V_G, T)$ fit very well to the function
form of Poole-Frenkel (PF) conduction over a wide range of bias and temperature.

PF conduction is governed by

\[ I_D(\Delta V, T) = a \Delta V \exp[(b(\Delta V/d)^{1/2} - c)/k_B T] \]  

(3.1)

where a, b, c and d are all positive constants [41, 42]. The PF fitting is shown in Figure 3.6, where plots of \( \ln (I_D/\Delta V) \) versus \( \Delta V^{1/2}/T \) produce a family of straight-line curves at each measurement temperature.

![Figure 3.6: Poole-Frenkel Plot of \( I_D(V_D, V_G, T) \) (points) and fitting (dashed lines)](image)

3.7 Poole-Frenkel conduction at single defect limit

To understand the relevance of Equation 3.1, we first discuss conventional PF conduction. Conventional Poole-Frenkel conduction is modeled for Metal-Insulator-Metal (MIM) junction with 2D interface. Perfect insulators only conduct via tunneling, but localized defect states
provide additional resonant-tunneling pathways through thin, imperfect insulators. The unbiased and biased situations are depicted by energy diagrams in Figure 3.7(a) and Figure 3.7(b), respectively.

Each localized trap state is characterized by a Coulomb barrier $\Phi_0$ in an insulating film of thickness $D$ and dielectric constant $\varepsilon$. When the junction is biased by metallic or semiconducting contacts on either side, the applied field $F = \Delta V/(D\varepsilon)$ lowers the barrier to $\Phi = \Phi_0 - eF$ and reduces the effective escape width to only $x_0$. In PF conduction, carriers tunneling into the trap from the left contact escape over $\Phi$ by either thermal or field-assisted emission. The PF model is easily extended to ensembles of traps having broad energy distributions and can be relevant for insulators up to 300nm thick[43, 44]. The parameters $c$ and $d$ in Equation 3.1 correspond to $\Phi_0$ and $\varepsilon D$, respectively, and PF plots like the one shown in Figure 3.6 can be used to extract experimental values of $\Phi_0$ that are typically 1 to 2 eV[43, 44].
Figure 3.7: Band Diagrams illustrate the onset of Poole-Frenkel conduction occurring in one and two dimensional systems. In each case, $E_0$ is the trap depth, $\Phi$ is the effective barrier height, and $L$ is the characteristic length, $X_0$ is the trap width, $E_F$ is the fermi energy, $E_V$ is the valence band, $E_C$ is the conduction band and $E_*$ is a high energy band. While the MIM panels illustrate electron-type conduction, the energy scale for the SWCNT panels has been reversed in order to illustrate hole-type conduction.

A point defect in a 1D SWCNT is certainly different from a 2D insulating barrier, and its geometric width $D$ is vanishingly small. Nevertheless, a simple electrostatic model suggests why PF mechanisms still apply. The coulomb potential of a charged defect is virtually unscreened by the exceptionally small, 1D carrier densities of SWCNTs. According to theoretical calculations, a depletion zone is induced with a width that can exceed 1.0 μm[45, 46]. The corresponding band diagrams, inverted for the electrons in Figure 3.7(c) and Figure 3.7(d), respectively, are very similar to the conventional Poole-Frenkel diagrams.

This explanation predicts that fits to Eq. 3.1 depend on the carrier depletion width rather than the physical extent of the defect itself. Indeed, fitting SWCNT data within the PF framework of Eq. 3.1 produces large $D$ values that match the KPFM imaging. More pre-
cisely, the region of high electric field $\Delta V/\varepsilon D$ in the KPFM data of Figure 3.3b extends for 0.9±0.1 m. The PF slopes in Figure 3.6 gives value of $\varepsilon D=2.8±0.4$ m. Assuming a dielectric constant $\varepsilon=2.5$ intermediate between air and SiO$_2$, this gives a width $D = 1.1±0.2$ m that closely matches the KPFM measurement. Such large values were discounted as unphysical in the first such report [47], but subsequent researchers have repeatedly shown that highly disordered and damaged SWCNT films fit PF conduction models [48, 49, 50, 51, 52]. Figure 3.6 now proves that Eq. 3.1 is the appropriate description of defect scattering in a SWCNT and that PF conduction does not arise from the morphological disorder found in processed SWCNTs, entangled SWCNT films or SWCNT composites.

Theory predicts that SWCNT screening lengths should depend sensitively on carrier density. Because of the doping effect of back gate bias on SWCNT, the charge carrier density can change by shifting back gate bias. Figure 3.8a shows $D$ values from PF fitting over a range of $V_G$ values in a single device. On either side of the conductance minimum at $V_G = -1$ V, $D$ increases to values as high as 2.5 m. The coulomb scattering barrier height $\Phi_0$ can be extrapolated from parameter $c$ from Eq. 3.1 by fitting the intercepts in Fig. 3.6 versus $1/k_B T$. Fig. 3.8b shows that $\Phi_0$ varies from 17 meV to 35 meV, which is significantly lower than conventional PF conduction.
Thus, the PF model needs substantial modifications to apply directly to 1D SWCNTs. The conventional form in Eq. 3.1 has no explicit dependence on carrier density nor $V_G$, since neither of these is relevant for determining the field $F$ across a 2D insulating film. In 1D, trap emission still depends exponentially on $F$, but $F$ also depends on net charge of the defect site, which for a chemical adduct with a given electronegativity might be a fractional charge.

Another example shows how PF conduction is sensitive to back gate bias. In Fig. 3.9, when $V_G = -10 \text{ V}$, charge carriers are scattered the most, the conductance drops more than 50%. After the $\Delta V$ is calculated by careful subtraction of pristine $I_D(V_D, V_G = -10V, T = 100K)$ from $I_D(V_D, V_G = -10V, T = 100K)$ after functionalization, the plot follows a fairly good linear fit as shown in the inset of Fig. 3.9b. With data from other temperatures combined, $\Phi_0 = 23 \text{ meV}$ can be extrapolated. However for $V_G = +10 \text{ V}$, the defect is virtually transparent to charge carriers, the voltage dropped around the defect is zero.
Figure 3.9: PF conduction of another damaged SWCNT device with extreme sensitivity on $V_G$ (a) PF plot of pristine (Black) and post-functionalization (Red) at $V_G = +10$ V; (b) PF plot of pristine (Black) and post-functionalization (Red) at $V_G = -10$ V. Inset: PF plot after careful subtraction of pristine from post-functionalization data.
Chapter 4

Nanoscale SWCNT/Cu composite

4.1 Introduction

Reducing weight is a never-ending challenge in the aviation industry, and the latest jumbo aircraft models and high fuel prices are placing even more pressure on aircraft companies to find ways to reduce aircraft weights. Electrical cables offer much promise for weight reduction because they have not changed much in the past decades. Recently, carbon materials have attracted a lot attention in the aviation industry due to their low weight and high strength. In 2013, NanoComp received millions in funding from the Department of Defense for their project to develop CNT materials for the next generation of electrical conductors. Airbus has been supportive of graphene research program for similar applications.

However, the reported resistivity of CNTs is around $1 \, \Omega \cdot \text{m}$ [53, 54], but the resistivity of Cu at 20 °C is $16.78 \, \text{nΩ} \cdot \text{m}$. So in term of good electrical conductors, Cu is still superior to SWCNTs even though SWCNTs have the advantage of reduced weight.

In 2013, Hata’s group reported a new composite of CNTs and Cu with the ratio of 55% and
The research concluded that this Cu/CNT composite had similar conductivity to pure Cu at room temperature, and at around moderately elevated temperatures (75 °C) the conductivity of this composite was even higher than pure Cu. If true, this finding would be quite a leap forward, because this highly conductive composite cuts the mass by half.

This research showed that a composite of Cu and CNTs may be the solution for the next generation light-weight electrical conductor. If the aviation industry eventually replace traditional Cu by this novel composite, they could reduce weight by almost 50% and still provide the same high conductivity. By just replacing the electrical cables in an aircraft, hundreds to thousands of pounds of fuel per aircraft could be saved annually. This improvement could mean millions of annual cost reduction.

Hata et. al. also found that their composite had an 100 fold increase of ampacity compared to Cu.[55] The development of modern electronic devices is undergoing a trend of miniaturization which requires higher and higher ampacity to keep pace with this trend. It is predicted that in 2015 the current density in devices is expected to exceed the breakdown limit of Cu wires.[21] The Cu/CNT composite can sustain higher current density and solve this problem.

While Hata’s findings were promising, the work did not explain why CNTs in this composite had similar as or even higher conductivity than Cu conductivity. The experiment in this chapter used nanoscale Cu/CNT composites to understand the mechanism. In bulk Cu/CNT composite, the CNTs are not orienting in the same direction, and Cu around each CNTs does not have same thickness. This brings up challenges for future theoretical modelling. Instead of characterizing bulk Cu/CNT composite, this research electrodeposits Cu onto individual SWCNT to obtain nanoscale composite. This is a much simpler configuration for understanding the physics. This chapter focuses on obtaining thin, smooth and conducting Cu layers on SWCNT using electrodeposition and then electrical measurement on this nanoscale
4.2 Electrodeposition on SWCNT

There has been a lot of previous research on electrodeposition onto SWCNTs, including electrodeposition of various metals and metal oxides. The easiest type of electrodeposition is for oxides. The Collins group demonstrated that MnO$_2$ could be deposited on SWCNT well and controllably.\cite{56, 57} Figure 4.1a shows an example of MnO$_2$ nucleated conformally on SWCNTs with good thickness control. Figure 4.1b shows MnO$_2$ coating thickness versus deposition time. The deposition rate was approximately 1.3 nm/s to 2.5 nm/s, depending on the presence of LiClO$_4$ in the electrolyte.

Due to SWCNTs’ relatively inert and hydrophobic surface, SWCNTs are poor substrate for many types of electrodeposition. Most metals cannot be deposited well on SWCNTs. Metals do not wet SWCNTs or freely nucleate deposit on SWCNTs. Previous research demonstrated that metal perfectly nucleates on contaminant and defects, rather than on SWCNT pristine sidewall, by a potential difference of about 200 meV.\cite{?} Metal such as Ag, Ni, Pt and Pd all been showed to have ‘‘random” nucleation on SWCNT during electrodeposition as shown.

![Figure 4.1: (a)SWCNT device with smooth MnO$_2$coating (b) MnO$_2$ deposition trend][56, 57]
in Figure 4.2a. Day et. al. did comprehensive research on Pt and Pd deposition on CNT networks. They varied the deposition time and deposition driving force to vary the parameter of metal nanoparticle's size and density, but no continuous metal deposition was achieved. Identical effects was observed for electrodeposition on graphite edges a decade ago.

Figure 4.2: Defect and contaminant-initiated nucleation and growth of metal electrodeposits on CNTs (a) Ni deposition on single SWCNT (b) Pt electrodeposition on network of CNTs with variation of deposition time and potential

### 4.3 Three-terminal electrochemistry

The electrodeposition was performed in the same type of miniature electrochemical cell described in Chapter 2. In order to deposit metal onto SWCNTs, a positive potential relative to the SWCNT WE was applied to the CE by Keithley 2400 output.

During electrodeposition, current flowing into the WE was measured by a preamplifier (Keithley 428). The potential of the RE and the CE and the electrodeposition current...
were acquired using data acquisition hardware (DAQ) from National Instruments.

4.4 Modified device configuration

Conventional SWCNT devices have lithographic source and drain electrodes that are hundreds of microns long. The resistance of these metal electrodes are 100 Ω ~ 1 kΩ, for typical cross-section of 2 m × 40 nm. For a 2 m-long SWCNT device, the SWCNT resistance is 100kΩ ~ 10MΩ or even higher. The resistance of metal electrodes is less than 1% of SWCNT resistance, and negligible.

SWCNT with Cu coating, have much lower resistances. For Cu nanowires with a diameter of 40 nm, the resistance is about 26.7 Ω, which is even lower than the connecting electrodes’ resistance. Therefore, the resistance of Cu-coated SWCNT can not be measured using two-terminal I-V measurement.

Figure 4.3 shows a design of SWCNT devices, called DPA wafer design, specially designed for low conductance nanoscale devices. This DPA design connects SWCNT devices with a 4-terminal configuration. By separating the voltage sensing and current carrying electrodes, device resistance can be measured more accurately and without the electrode and contact resistances. In the DPA design, each metal electrode is directly connected to the opposite electrode, and each SWCNT device is connected to 4 different electrodes. For example, in Figure 4.3, electrode “a” is connected with “b” and same for “c” with “d”. For the SWCNT connects “a” and “c” also connects with “b” and “d”, thus a 4-terminal configuration. With this design, the error bar of resistance is below 0.01 Ω, even though it is measured through electrodes with kΩ resistance.
4.5 Aqueous Cu electrodeposition

Aqueous CuSO₄ solution is the most commonly used electrolyte for Cu electrodeposition in both scientific research and industry. For this project, the electrodeposition electrolyte was 100 mM CuSO₄ without any extra additive. The concentration was high enough to make sure that the deposition was not diffusion limited. Commercial Cu deposition solution was considered at the beginning of this project, however concerns about extra surfactant or additives affecting the electrical conductance led us to work with pure CuSO₄.

Just like with other metal depositions on SWCNTs, Cu nucleation is favored on contaminants and defects rather than the sidewall. If the deposition potential is not negative enough, only defects and contaminants nucleated Cu, but other portions of the SWCNT remain deposition-free.

To solve this challenge, a bi-potentiostatic deposition strategy was used. The strategy was depositing Cu with a more negative deposition pulse to nucleate on every portions of SWCNT and followed by a less negative deposition pulse of gap-filling process. This is a common method in industry called a “strike”. A “strike” is a special plating deposit at high current density.
density that forms a thin plating with high quality and good adherence to the substrate. The more negative deposition pulse provides a higher nucleation density, and the following less negative potential has a slower deposition rate with uniform coating. In order to make the thin Cu stripe electrically conductive, the deposition has to be gap free. The less negative deposition fill up all the gaps.

Figure 4.4a shows a good example of random nucleation on SWCNT. A minor bias (\(V_D = 0.01\) V) was applied across the SWCNT. During the deposition, only nucleation pulse (-0.7 V vs. Ag/AgCl) was applied for 20 ms. In the picture, the sample was passivated with photoresist PMMA with a square window in the center exposing the SWCNT as well as the top and bottom electrodes. On the SWCNT there were a few nanoparticles deposited on the surface and also on the bottom electrodes there were roughly 15nm Cu deposition. However on the top electrode, no such deposition was observed. It was probably because that the deposition potential ( -0.7 V vs. Ag/AgCl) was on the threshold of just being able to nucleate on Pd electrodes, and because the top electrode had less potential difference to the electrolyte, no nucleation on the top electrode was obtained.

Figure 4.4: Aqueous Cu deposition on SWCNTs (a) Selective deposition of Cu nanoparticles on SWCNT due to deposition voltage \(V < 0.5\) V (b) Smooth Cu coating on SWCNT using an initial strike deposition voltage \(V = 0.8\) V

Figure4.4b shows a successful nanometer scale Cu deposition on SWCNT. The deposition potential was \(V = -0.85\) (vs. Ag/AgCl RE) for 20 ms, followed by deposition potential \(V = -0.4\)
V for 12 seconds. At a deposition potential of -0.4 V, Cu deposition rate was low. This rate fills the gaps between Cu nucleate particles filled without growing the Cu film too fast. In 4.4b, the Cu coating was 170 nm thick, which means the deposition rate at -8.5 V was about 8.5 nm/ms.

In order to achieve a higher carbon ratio in the nanoscale SWCNT/Cu composite, the Cu thickness needs to be as low as 2 to 10 nm. To obtain a Cu film as thin as 10 nm, the density of nucleation is a critical parameter. Low nucleation densities will leave gaps in the film. The strategy was raising up the nucleation density by lowering the deposition potential even more, so that the nucleations would form a smooth and conducting coating and minimize or even eliminate the gap filling process.

However, a even lower deposition potential on SWCNT caused hydrogen evolution on the sidewall. When the deposition potential was lower than -0.9 V, there was H\textsubscript{2} produced on SWCNT, separating SWCNT from the electrolyte and stop electrodeposition locally. The lower deposition potential it was, the bigger and faster the hydrogen bubbles generated, and the rougher Cu coating was. Figure 4.5 shows Cu coating with roughness over 20nm, at deposition potential of -0.95 V.

![Figure 4.5: Cu electrodeposition on SWCNT with H\textsubscript{2} evolution](image-url)
4.6 Non-aqueous Cu electrodeposition

Because of the presence of H$^+$ in aqueous electrolyte, hydrogen evolution prevents lowering the negative deposition potential on SWCNT. Polar aprotic solvents are non-aqueous solvents that dissolve many salts but lack an acidic hydrogen. Therefore, non-aqueous electrodeposition helps to increase the nucleation density without producing H$_2$.

Multiple aprotic solvents were tried. Acetonitrile was the first that was considered. Because of acetonitrile’s low molecular mass and low boiling temperature, it evaporated too fast in air. In this research, the electrodeposition was performed in a micro electrochemistry cell, with only a tiny droplet gently touching the surface of SWCNT. In a few seconds, all the acetonitrile evaporated and all salt dissolved coated on the surface.

Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are both colorless polar aprotic solvents, with higher boiling points. In air, both solvents evaporate slowly. Both DMF and DMSO dissolve both polar and nonpolar compounds and are miscible in a wide range of organic solvents as well as water. Previous research showed that DMF is a great solvent of generating CNT dispersions due to great absorption of DMF on CNT surface.[60, 61] This could help metal nucleation on SWCNT sidewall. Therefore DMF was used in this project as the solvent.

Anhydrous cupric acetate (Cu(OAc)$_2$) is very soluble in DMF. 0.1 M Cu(OAc)$_2$ in DMF was used, with no supporting electrolyte or other additives.

A standard Ag/Ag RE does not work well in a non-aqueous solution. A Ag/AgCl RE is a Ag/AgCl wire submerged in 3M aqueous KCl solution. Instead of a standard Ag/AgCl RE, a non-aqueous Ag/Ag$^+$RE was used. A used Ag/AgCl RE was recycled by removing the Ag/AgCl wire and replacing it with Ag wire. The Ag wire was submerged in 0.1M AgNO$_3$ in DMF solution in a PTFE tubing.
Figure 4.6 shows 2 great examples of Cu coated SWCNT from non-aqueous electrodeposition. Figure 4.6a shows a SWCNT device with Ti electrodes with Cu coatings on the SWCNT and on the electrode edges. During the electrodeposition, a single square pulse of 2.5 V (Pt RE) with duration of 200 ms was applied on the CE and a small bias of 10mV was applied across the SWCNT. A smooth Cu film was coated on SWCNT, but the thickness gradually decreased from the top end (90 nm) to the bottom end (50 nm). The variation of thickness was due to the bias applied across the SWCNT and higher potential difference from SWCNT to electrolyte at the top end. Figure 4.6b shows another SWCNT device with Ti electrodes had about 40 nm thick Cu film coating. The electrodeposition was a square pulse of 1.7 V (Pt RE) with duration of 2 s.

Without using a “strike” bi-potential method, the non-aqueous electrodeposition obtains thinner Cu film than in aqueous solution. In non-aqueous deposition, the nucleation density was higher and required no additional gap-filling process. Comparing the deposition result of the two method, the deposition rate in non-aqueous solution was 1000 times lower than in aqueous. The deposition in non-aqueous solution was therefore more controllable.
4.7 Electrical characterization of Cu coated SWCNT

In spite of the difficulties to get very thinly Cu coated SWCNT, one SWCNT device with 300 nm to 400 nm thick Cu coating from aqueous solution was obtained. The deposition potential was -0.75V (vs. Ag/AgCl) for 50msec, and then 0V (vs. Ag/AgCl) for 5sec.

After the deposition, the resistance of Cu coated SWCNT was probed in the Desert probe station to be 1.04Ω. Because Cu is vulnerable to be oxidized, the obtained Cu film here was expected to be a mixture of Cu and CuO$_x$. Theoretical calculation predicted that pure Cu with same dimensions should be 0.14 Ω, which stood by the assumption of presence of CuO$_x$. Therefore, before the measurement of the composite conductance, anneal to reduce Cu oxide was necessary.

After the deposition was finished, a series of anneal including annealing in vacuum and annealing with low pressure hydrogen were performed, after each anneal, the composite resistance was probed. Table 4.1 shows each anneal’s condition and the composite resistance after each anneal. From anneal #2 to anneal #7 in Table 4.1 and resistance measurement were all performed in sequence in Desert probe station. Because the thermocouple in the cryogenic chamber can only work between 4K to 475K, so the highest anneal temperature in this chamber was only as high as 190 °C (463K). Anneal #8 was performed in CVD furnace as described in Chapter 2. Further anneal on this composite was tried at more elevated temperature (350 °C) and longer time (1 hr), but the Cu/SWCNT composite became disconnected after the anneal. It was attributed to insufficient Ar purge so that there was still small amount of oxygen left in the furnace which resulted in oxidizing Cu and SWCNT.

Table 4.1 shows that the composite resistance decreased as the annealing time and temperature increased and the presence of H$_2$ during anneal helped decreased the resistance as well. Each of the anneal runs reduced some Cu oxides and lowered the resistance. After all anneal runs and before the device was blown out, the resistance is as low as 0.465Ω, which was 3
times as high as pure Cu nanowire’s resistance with same dimension.

<table>
<thead>
<tr>
<th>Anneal Condition</th>
<th>Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 No Anneal</td>
<td>1.04 Ω</td>
</tr>
<tr>
<td>2 anneal in vacuum at 100 °C for 30 min</td>
<td>0.910 Ω</td>
</tr>
<tr>
<td>3 second anneal in vacuum at 100 °C for 30 min</td>
<td>0.807 Ω</td>
</tr>
<tr>
<td>4 anneal with 8.9 Torr H₂ at 100 °C for 60 min</td>
<td>0.768 Ω</td>
</tr>
<tr>
<td>5 anneal under vacuum at 150 °C for 45 min</td>
<td>0.629 Ω</td>
</tr>
<tr>
<td>6 anneal under vacuum at 150 °C for 50 min and 180 °C for 10 min</td>
<td>0.605 Ω</td>
</tr>
<tr>
<td>7 anneal with 15 Torr H₂ at 150 °C for 50 min and 190 °C for 10 min</td>
<td>0.530 Ω</td>
</tr>
<tr>
<td>8 anneal under 99% Ar and 1% H₂ at 300 °C for 10 min</td>
<td>0.465 Ω</td>
</tr>
</tbody>
</table>

Table 4.1: Table of resistance after each anneal conditions in sequence

Because this preliminary Cu/SWCNT had a very high Cu ratio, it should have a conductivity closer to Cu conductivity. There are a few possible reasons for the Cu/SWCNT composite’s high resistivity. First, there could be Cu oxides in the composite, because from the trend in Table 4.1, the resistance was continuously going down with higher temperature and longer time. The last anneal was only 10 minutes. It was unfortunate that when 3 hours anneal, as mentioned in previous research[55], was tried, the composite was blown out, and we did not have a chance to measure the resistance after this anneal. The resistance could go much lower if we did anneal with much longer time. Second, during aqueous deposition, nucleation density on SWCNT was relatively lower than non-aqueous. When Cu starts to fill up the gaps between nucleations, there can be grain boundaries between each emerging Cu nucleation. As research revealed, each grain boundary add additional 69 mΩ to the total resistance.[62] If all additional resistance come from grain boundaries, that means only 5 grains, which is very possible to happen.

When the composite was still in the vacuum cryogenic chamber, we measured the resistance
at different temperatures as it was cooling down from the peak temperature of annealing. To compare with Hata’s result, the conductance of this nanoscale Cu/SWCNT composite was plotted versus temperature in the same graph in their journal. Figure 4.7 shows the conductance dependence on temperature of pure Cu, bulk Cu/CNT composite[55] and nanoscale Cu coated SWCNT. Bulk Cu/CNT composite had similar conductance as pure Cu, but nanoscale Cu coated SWCNT had lower conductance than the other two materials. But the overall trend of temperature dependence was the same when comparing the curve of nanoscale Cu/SWCNT composite and that from bulk Cu/CNT composite. It indicated that SWCNT played an essential role in the composite conductance’s temperature conductance, in both cases of nanoscale and bulk Cu/CNT composites.

Figure 4.7: Conductance versus Temperature of pure Cu (Black), Hata group’s bulk Cu/CNT composite (Red) and our Cu coated SWCNT(Green)
4.8 Summary

This research was trying to obtain a nanoscale Cu/SWCNT composite to understand the mechanism of the composite’s reported high conductivity. The ideal nanoscale Cu/SWCNT composite to compare with bulk composite would be a 2 nm to 10 nm smooth and conducting Cu film coated SWCNT. But it’s difficult to obtain smooth Cu coating, let alone nanometer thin.

Both electrodeposition in aqueous and non-aqueous solution were tried and it turns out that deposition in non-aqueous was superior. The nucleation density was critical to obtain thin and smooth Cu coating. Due to hydrogen evolution, nucleation density in aqueous solution was much lower than nucleation density in non-aqueous. Plus, the deposition rate in non-aqueous is 1000 times lower than in aqueous. The obtained lowest Cu film on SWCNT sidewall was 40 nm.

A composite from deposition in aqueous deposition was obtained, but even with multiple anneal, the resistance of the nanocomposite was 3 times higher than pure Cu. It indicated that SWCNT played an essential role in the composite conductance, especially conductance’s temperature conductance, in both cases of nanoscale and bulk Cu/CNT composites.
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