CHARACTERIZATION OF ELECTRICAL CONDUCTIVITY OF CARBON FIBER/EPOXY COMPOSITES WITH CONDUCTIVE AFM AND SCANNING MICROWAVE IMPEDANCE MICROSCOPY

BY

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THESIS

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Abstract

This thesis investigates the electrical conductivity of IM7 carbon fibers using two Atomic Force Microscope (AFM)–based techniques: Conductive AFM (C-AFM) and Scanning Microwave Impedance Microscopy (sMIM). Unidirectional IM7/977-3 carbon fiber/epoxy laminates were manufactured and examined with these two techniques. C-AFM was used to measure the bulk resistivity of IM7 fibers at $(1.9 \pm 1.1) \times 10^{-3} \, \Omega \cdot \text{cm}$. Given that the uncertainty of these measurements is rather large, implementation of calibration experiments is needed. sMIM experiments revealed large nano-scale spatial variations in the axial and transverse conductances of IM7 fibers. Attempts were made to quantify sMIM results through construction of experimental and computational calibration curves, but neither of these efforts was successful in yielding conductivity measurements that agreed with the measurements made with C-AFM or the manufacturer specification. Refinements to the computational methodology such as improved material property inputs and better isolation of the sMIM signal could yield promising future results for sMIM characterization of conductivity.
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Chapter 1: Introduction

1.1 Composite Materials in Aerospace Engineering

Fiber-reinforced composite materials are used in a wide array of industries for their excellent mechanical properties. Their high specific strength and stiffness translate into structural materials that provide high performance at a reduced weight. Their fatigue tolerance, chemical resistance, lack of corrosion, and ability to be designed and tailored for specific applications, among other qualities, make them desirable for advanced structural engineering applications. These factors have made these materials ideal for use in the aerospace industry, where a premium is placed on reducing weight and increasing performance.

The first uses of composites in the aerospace industry can be traced back to early glass fiber reinforced plastic aircraft components in the 1940s.\(^1\) Over time, the growing recognition of composite materials’ advantageous properties correlated with increasing usage in aerospace designs. In the 1980’s, the Northrop Grumman B-2 Spirit stealth bomber was manufactured using a largely carbon fiber composite design for its beneficial mechanical properties and excellent stealth abilities.\(^2\) The most modern example of composites use in aerospace engineering is the Boeing 787 in which fully 50% of the material weight is composite material. As a result of its reduced weight the aircraft is able to achieve a 20% increase in fuel efficiency.\(^3\)

1.2 Electromagnetic Properties of Composite Materials

The application of composite materials in the aerospace industry is largely driven by mechanical performance (e.g. specific stiffness). However, multifunctional applications are increasingly important in which structural performance is combined with secondary
functionality. In this work we are motivated by the investigation of electromagnetic properties of carbon fiber/epoxy composites. The two main electromagnetic properties of general interest are permittivity (or dielectric constant) and electrical conductivity. The permittivity of carbon fiber composites has been the subject of a variety of experimental and computational analyses.\textsuperscript{4,5,6} The permittivity of composites is of great interest to the aerospace industry for its effect on performance in electromagnetic interference (EMI) shielding\textsuperscript{7} and radar absorption.\textsuperscript{8} Understanding of the electrical conductivity of composites similarly has great utility in applications such as structural health monitoring\textsuperscript{9} and aircraft lightning strike protection.\textsuperscript{10}

The majority of recent investigation of electrical conductivity of carbon fiber composites, though, has been restricted to studies for applications, and more fundamental research on electrical conductivity of single carbon fibers has been limited to interrogating bulk resistance (or conductance) and resistivity (or conductivity).\textsuperscript{11,12,13,14} However, carbon fibers are known to be anisotropic with a preferred orientation of turbostratic graphite crystals.\textsuperscript{15} Thus, the electrical conductivity of carbon fibers should be anisotropic as well, and bulk measurements provide little insight into their use in fiber-reinforced composites. Work in this realm has been mostly limited by a lack of experimental techniques capable of examining the anisotropic features of carbon fibers. This work implements new experimental techniques for bulk and local conductivity characterization to examine the conductivity of carbon fibers.

1.3 Experimental Techniques for Conductivity Characterization

The goal of this work is to experimentally measure conductivity of carbon fibers with two-dimensional spatial resolution. There exist only a few experimental techniques for measuring material conductivity. These techniques can be generally separated into two categories: contact methods and non-contact methods.
The two most well-known and widely used contact methods are called 2-point probe and 4-point probe. 2-point probe involves two electrodes being adhered to opposite sides of a block of material, usually a rod or rectangular prism, and applying a known voltage or current across the material. A schematic of a 2-point probe experiment is shown in Figure 1.

![Figure 1: Schematic of 2-point probe setup. Current is run along the length of the specimen, l, and current and voltage are measured with the same terminals at the two ends.](image)

Application of voltage or current and measurement of the other yields the resistance of the material, and the resistance can be used to determine the resistivity (or conductivity) of the material. The 2-point probe technique is often used with simple geometries, such as rods or rectangular prisms, since the length and cross-sectional area of the sample are well controlled.

The 4-point probe technique is similar in concept, but it uses four terminals instead of two. The four probes can be arranged in a variety of geometries, but they are often placed in a straight line with some known spacing between the probes (Figure 2).
In 4-point probe testing, a current is applied between the two outer probes while the two inner probes measure the resulting voltage drop. This technique is advantageous for its ability to eliminate contact resistance present in 2-point probe measurements. In 2-point probe testing, charges accumulate around the current-applying probes and change the measurement of voltage through those same probes. Contact resistance is particularly likely to occur in small or thin film materials where the material volume through which charge can move is small. The 4-point probe technique circumvents this issue by separating the current-applying and voltage-measuring probes and eliminating contact resistance. This technique is commonly used on thin films and semiconductors.\textsuperscript{17}

Conductive Atomic Force Microscopy (C-AFM) is another contact method for measuring electrical conductivity. C-AFM involves the use of an Atomic Force Microscope (AFM) where a small cantilever (~ 450 \(\mu\)m long) with a pyramid shaped tip at its end (apex radius ~ 10-50 nm) is scanned across a material in a raster-like motion, with the cantilever applying a known force to the material, to obtain a topological map of a material surface. C-AFM uses a metal-coated cantilever to conduct current through the tip into the sample. The process through which C-AFM
is able to measure the conductivity of a material is the same as for 2-point probe, but done on a much smaller scale.\textsuperscript{18} This technique has been utilized to measure the resistivity of nano-scale materials such as carbon nanotubes (CNT’s).\textsuperscript{19} C-AFM has also been used to qualitatively examine the conductivity of a short carbon fiber-reinforced composite.\textsuperscript{20} This technique was utilized here to measure the bulk conductivity of single carbon fibers.

A similar technique to C-AFM is Scanning Tunneling Microscopy (STM), a non-contact method. STM also uses the platform of AFM to scan across the surface of a material, but instead of contacting the sample with a fixed force, STM holds the cantilever several angstroms above the material surface, causing electron tunneling between the conductive tip and biased sample. There are two modes of operation: constant current and constant height operation. In constant current operation, the tunneling current is held constant and the cantilever height above the sample will change with topography to maintain the desired current. In constant height operation, the height of the cantilever above the sample is fixed, causing changes in the tunneling current when the tip is scanned over the varying topology of the sample. The variations in height or current can be related to changes in charge density and density of states of the material; these quantities can be used to calculate the changes in conductivity. Drawbacks of STM, though, include the need for a completely conductive sample and the coupling between current and topology, which prevents STM from obtaining simultaneous topology and current mapping possible with C-AFM.\textsuperscript{21,22}

A very recent advancement in non-contact conductivity measurements is called THz time-domain spectroscopy. This technique uses lasers to impinge a material with terahertz electromagnetic radiation; the reflection of this radiation is measured, and the differences between the transmitted and received waves can be used to evaluate material properties such as
conductivity. This technique was first used to evaluate the conductivity of CNT thin films deposited on fused-quarts substrates. It has only been used to evaluate the properties of thin films, though, and has not been used to examine individual micro- and nano-scale materials of interest. This technique is an unique method for non-contact evaluation of material conductivity, but the size scale of interrogation is too large for this work.

The final technique for evaluating material conductivity is called Scanning Microwave Impedance Microscopy (sMIM). It can be considered a combination of contact and non-contact methods, as it is an AFM-based technique that can operate in both contact and tapping modes. It operates similarly to traditional AFM, with the tip scanning over the material in a raster-like motion. However, an electromagnetically shielded tip is used to transmit a microwave that travels through the tip, interacts with the sample, and is reflected back to the tip. Similar to the THz laser method, the difference between the transmitted and received microwave signals can be analyzed to yield information about the material conductivity. Unlike the THz laser method, this technique operates at very small scales, with spatial resolution of electrical measurements on the order of the tip size, ~50-100 nm. Thus, this technique is capable of revealing micro- and nano-scale spatial variations in electrical conductivity. However, this technique, still being in its nascent stage, does not have the capability to readily make quantitative measurements. Regardless, this technique was selected for use in these studies because of its unique ability to examine micro- and nano-scale local variations in electrical conductivity. sMIM also provides a logical compliment to the bulk conductivity measurements to be done with C-AFM, as both are AFM-based techniques.
1.4 Project Objective

The objective of this thesis is to experimentally measure the conductivity/resistivity of carbon fibers with two-dimensional spatial resolution; this work will use IM7 carbon fibers. Chapter 2 describes how C-AFM is used to measure the bulk resistivity of single IM7 fibers in a unidirectional laminate. Chapter 3 details how sMIM is utilized to examine local, spatial variations of conductivity on carbon fibers. An attempt is made to quantify conductivity measurements with sMIM using two different methods: construction of an experimental calibration curve and modeling of the sMIM tip-sample impedance. Chapter 4 examines the successes and shortcomings of these conductivity measurement techniques and provides potential solutions to ongoing research questions.
Chapter 2: Conductivity Measurements with Conductive AFM

2.1 Introduction

Atomic force microscopy (AFM) is a scanning probe microscope technique that characterizes the surface topology of materials and has the ability to measure a variety of additional material properties at the micro- and nano-scales. AFM scans a cantilevered arm with a pointed tip at its end across a material in a raster-like motion. The movement of the cantilever in all three directions is controlled through precise actuation of piezoceramics. The instrument first performs a single line scan by moving the tip at across a material surface in a straight line. The distance and height travelled by the tip are recorded during each line scan, yielding the two-dimensional topology of the material along that line. The instrument performs successive line scans to create a three-dimensional surface topology map (see Figure 3). The cantilever is roughly 450 µm in length, 50 µm in width, and 2 µm in thickness, with the tip radius varying between 10 and 50 nm. There are a variety of AFM “modes” where the AFM performs further operations to obtain various types of other information in addition to surface topology.\textsuperscript{18}
One AFM mode is Conductive AFM (C-AFM). In this AFM mode, a voltage is applied between a metal-coated, conductive AFM tip and the sample. C-AFM operates in the same way as traditional AFM by collecting topology information, but it adds additional functionality and information by applying a voltage bias to the tip and running current through the material being
scanned. This function can be used to measure the resistivity (or conductivity) of the sample being scanned.

The method for measuring the resistivity of a material with C-AFM is schematically shown in Figure 4. An insulating material (white) contains an embedded conductive material (yellow) extending through the entire sample thickness. Silver paint or another conductive adhesive adheres the sample to an insulating substrate, shown in the figure as a glass microscope slide. A voltage is applied between the tip and the conductive silver paint electrode, and the cantilever scans across the material as it would with traditional AFM. When the tip scans over the insulating material, no current flows between the tip and the silver paint electrode. When the tip contacts the conductive material, an electrical connection is established between the tip and the silver paint electrode, and current is drawn through the conductive material. The location of the tip can be held fixed on the conductive material, and a voltage can be applied at the stationary tip to draw current through the conductive material. The applied voltage and resulting current are recorded to obtain a current-voltage response, called an I-V curve.
Figure 4: Schematic of C-AFM operation. (a): At cantilever location 1, the tip is in contact only with insulating material, and no current is drawn. (b): At cantilever location 2, the tip is in contact with a conductive material that makes contact with the silver paint electrode adhered to the glass slide. As a result, current is drawn through the system.

Simple mathematical analysis can be performed to obtain a material’s resistivity from an I-V curve. Ohm’s Law states
\[ V = IR \]  

where \( V \) is the voltage applied, \( I \) is the current drawn due to the applied voltage, and \( R \) is the material resistance. Rearranging Equation (1) yields

\[ \frac{1}{R} = \frac{I}{V} \]  

When an I-V curve is created with C-AFM, the slope, \( m \), of that curve is

\[ m = \frac{I_2 - I_1}{V_2 - V_1} \]  

where \( V_1 \) and \( I_1 \) are the voltage and current values at one given point on the I-V curve and \( V_2 \) and \( I_2 \) are the voltage and current values at another point. Considering that zero applied voltage induces zero current, if \( V_1 \) and \( I_1 \) are taken to be the points at the origin, then combining Equations (2) and (3) becomes

\[ m = \frac{I_2}{V_2} = \frac{I}{V} = \frac{1}{R} \]  

Thus, the material resistance is the inverse of the slope of the I-V curve.

While resistance gives insight into the material’s conductive capabilities, it is a quantity that includes both material property and geometry. To isolate the material property, it is more useful to examine the material resistivity. The relationship between resistance and resistivity is

\[ R = \rho \frac{L}{A} \]  

where \( R \) is the resistance, \( \rho \) is the material resistivity, \( L \) is the length along which current is being carried, and \( A \) is the cross-sectional area over which the current is travelling. Re-writing Equation (5) to isolate \( \rho \) and substituting in Equation (4) yields
\[ \rho = R \frac{A}{L} = \frac{1}{m} \frac{A}{L} \]  

(6)

Using Equation (6), the material resistivity can be calculated knowing the sample geometry and the slope of the I-V curve.

### 2.2 Materials and Methods

Carbon fiber/epoxy composites were manufactured for C-AFM experiments. The laminates were manufactured by Anthony Coppola (UIUC) using prepreg with IM7 PAN-based carbon fibers and 977-3 epoxy (IM7: Hexcel, 977-3: Cytec). The layup sequence was \([0]_{16}\), and the laminates were cured in an autoclave at 92.5 psi at 130 °C for four hours and then 170 °C for 3 hours. The resulting specimens were 3.5 mm thick. The samples were then cut with an Isomet diamond-tipped saw blade to be approximately 45 mm long. These samples were then turned on their sides, and their transverse (to the fiber orientation) cross-sections were polished to a maximum surface roughness of 0.05 \(\mu\)m. Once the samples were polished, they were then cut to the desired height by sectioning off material on the surface opposite the polished surface. Samples were cut to heights of 4.58, 6.03, 6.99, 8.55, and 10.19 mm. Figure 5 shows a schematic of a carbon fiber/epoxy laminate sample.
The samples were then prepared for C-AFM on glass microscope slides. A glass slide was placed on the lab bench, and a stripe of conductive silver paint (Ted Pella, Inc.) was painted onto the surface of the glass slide as shown in Figure 6a. Enough paint was applied to create a uniform thickness of silver paint on the slide. While the first application of paint was still drying, a larger, concentrated volume of silver paint was applied to one end of the stripe, and a small magnet was placed in this volume of paint as shown in Figure 6b.

The unpolished surface opposite the polished surface of carbon fiber laminate was then wetted out with silver paint and allowed to dry for five minutes. This bottom surface was once again coated in silver paint and the portion of the glass slide coated in silver paint was also repainted. While both applications of silver paint were still liquid, the carbon fiber laminate was placed on the glass slide with the two silver painted surfaces in contact. This methodology for wetting out the unpolished bottom surface of the laminate provided a strong electrical connection; failing to wet out the bottom of the laminate or not re-applying enough silver paint to the glass slide before joining the laminate often resulted in a poor electrical connection. Samples
were left in a fume hood for 24 to 48 hours to fully cure. The resulting specimens are schematically shown below in Figure 6c.

Figure 6: Schematic of C-AFM sample preparation. (a): Silver paint is applied to a glass slide. (b): A concentrated volume of silver paint is applied on top of the first silver paint application, and a magnet is placed in that concentrated volume. (c) Carbon fiber laminate is adhered to silver paint electrode with fibers in vertical (z) orientation.

After allowing the samples to finish curing, samples were tested in an AFM. All AFM work was done on an Asylum Research MFP-3D Atomic Force Microscope. C-AFM was carried out using the ORCA holder attachment in contact mode. Contact, Cr/Pt coated tips (Ted Pella, Inc./BudgetSensors) were used for all C-AFM testing. The sample was placed in the AFM, and the wire connected to the ORCA holder was attached to the magnet on the sample.
The tip approach was performed, and a 10 µm scan at 0.75 Hz with a 1V set point was executed. A 5 mV voltage was also applied to the sample with a -50 mV offset during this scan. When the tip scanned over an epoxy region, no current was drawn through the system because the epoxy is insulating. However, when the tip scanned over a carbon fiber, an electrical connection was made and drew current through the fiber.

After a scan was complete, current-voltage response curves, called I-V curves, were collected. A point was chosen on a carbon fiber, located with the completed area scan, and the tip was engaged at that point with a 0V sample voltage and -50 mV offset, i.e. the voltage drop across the sample was held at 0V with a -50 mV offset (accounting for a 50 mV system offset). The tip was held fixed at that location. Time-varying current fluctuations were frequently observed in the current meter in the AFM software when first engaging the tip on a carbon fiber; to minimize this effect, the tip was kept at the desired point for at least one minute prior to I-V curve data collection when unexpected fluctuations occurred. It was observed empirically that after some time with the tip being held fixed on the carbon fiber, the current fluctuations reduced to a minimum.

An I-V curve was collected after time-varying current fluctuations were at a minimum. One I-V curve contained information from four voltage sweeps. One voltage sweep consisted of the sample being driven through a voltage range, e.g. ±0.2 mV and the current drawn being measured. The voltage sweep frequency was between 0.5 and 1.0 Hz. Multiple I-V curves were collected at the same location without changing any parameters or disengaging the tip. At least five curves were collected at each location, at least two locations were measured for each fiber considered, and at least two fibers were examined for every sample.
Once collected, this data was reduced and analyzed with MATLAB scripts. The ORCA holder used was only capable of measuring currents within ±20 nA, and as a result, the data saturated at ±20 nA at the higher and lower voltage ranges examined. To analyze an I-V curve, the region of the curve where all four sweeps were not saturated at ±20 nA was examined. The data points over this region were averaged between the four sweeps, and a linear regression was performed to obtain the slope of this averaged data. Using Equations (4) and (6), the resistance and resistivity of the fiber examined were calculated.

I-V curves were collected for multiple samples of different fiber lengths to account for contact resistance. Because C-AFM is essentially a 2-point probe method, there is likely contact resistance associated with its measurements, and a well-known methodology was used to evaluate contact resistance.\(^{26,27}\) The resistance data for these samples with different fiber lengths were compiled on a plot of resistance vs. sample fiber length. Following from Equation (4), a plot of \(R\) vs. \(L\) should produce a straight line that intersects the origin, assuming constant material resistivity and cross-section. A line that does not intersect the origin indicates the presence of contact resistance, and the contact resistance is equal to the y-intercept of that line. Additionally, Equation (4) shows that a plot of \(R\) vs. \(L\) will have a slope equal to \(\rho/A\), thus producing Equation (7)

\[
\frac{m_{contact}}{A} = \frac{\rho}{A}
\]

where \(m_{contact}\) is the slope of the line in the \(R\) vs. \(L\) plot. Equation (7) can be rearranged to solve for the resistivity of the material while accounting for contact resistance, as shown in Equation (8).

\[
\rho = m_{contact}A
\]
Thus, this section presents two different ways of calculating the material resistivity: one using standard equations relating resistance and resistivity, and one accounting for contact resistance of the experimental setup.

2.3 Results and Discussion

Representative height and current traces from laminate area scans are shown in Figure 7 below.

![Figure 7: Representative height (a) and current (b) traces of unidirectional laminate. White regions indicate high current draw, while black regions indicate low current draw.](image)

The diameter of IM7 fibers is 5 μm. The white regions in Figure 7b indicate locations of high current draw, while the black regions indicate areas of low or no current draw. As expected, the fibers conduct a high level of current while the epoxy is insulating and conducts essentially no current.

A typical I-V curve and the bounds of the acceptable, non-saturated region are shown in Figure 8a. Figure 8b shows the averaged data and associated linear regression. The average is done point by point across all sweeps in the I-V curve, i.e. all current values at a given voltage
value are averaged together to obtain the average current for that voltage value. This is possible because measurements of current in all sweeps occur at the same voltages.

Figure 8: (a): Representative I-V curve with all four sweeps shown. Note that some of the sweeps are not entirely visible because other sweeps obscure their view. Also note that the dashed red lines indicate the selected bounds for averaging the data; the bounds were selected to only analyze the non-saturated region of the data. (b): Averaged I-V curve data with highlighted acceptable, non-saturated region and associated linear regression.
The resistivity values calculated from all I-V curves taken on a sample of given fiber length were averaged to obtain average resistivity values for each fiber length; those average values were averaged together to obtain the average resistivity of an IM7 fiber. This resistivity was calculated to be \((3.2 \pm 0.8) \times 10^{-3} \ \Omega \cdot \text{cm}\), where the uncertainty was calculated using the standard deviation of the data. However, the manufacturer specification for resistivity of IM7 fibers is \(1.5 \times 10^{-3} \ \Omega \cdot \text{cm}\).\textsuperscript{28} The analysis of the data in this manner does not agree with the manufacturer specification.

Using the methods outlined above for eliminating contact resistance, the following plot of resistance vs. fiber length was collected.

![Resistance vs. Fiber Length Plot](image)

Figure 9: Resistance vs. fiber length plot to evaluate contact resistance. The blue diamonds represent the average resistance values measured for carbon fibers of the given length, and the solid blue line is the linear regression of those average values. Extrapolating the average linear regression to zero fiber length shows a non-zero y-intercept, indicating the presence of contact resistance.
The blue diamonds indicate the average resistance value for each fiber length, the error bars represent ±1 standard deviation of the average values, and the solid blue line shows the linear regression of the average values. Note that if the linear regression of the average values were to be extrapolated to a fiber of zero length, there would be a non-zero y-intercept. As discussed in Section 2.2, this non-zero y-intercept indicates the presence of contact resistance. The contact resistance for this experimental setup was determined to be 960 Ω. The slope of the linear regression of the average values was 3.471 kΩ/mm with an $R^2 = 0.88$. Using Equation (8), the resistivity accounting for contact resistance was calculated to be $(1.9 \pm 1.1) \times 10^{-3}$ Ω*cm with the uncertainty being calculated from the slopes of the linear regressions of the average values ±1 standard deviation. This result agrees with the manufacturer specification of $1.5 \times 10^{-3}$ Ω*cm, although the uncertainty of the experimental data is quite significant.

The standard deviation of this resistivity data is rather large, 58% of the average value, but not unexpected for these types of measurements. The creation and execution of a control experiment would lend strong support to the validity of this result, particularly with its large uncertainty. An ideal candidate for a control experiment would be a homogenous and isotropic material with well-characterized conductivity, such as gold, silver, or aluminum. However, the ±20 nA constraint on C-AFM measurements limits the size of usable samples, and morphologies such as nanowires would need to be used. The work cited in Section 2.1 that analyzed the resistivity of carbon nanotubes lays a good groundwork for making resistivity measurements of nanomaterials using conductive AFM. The researchers utilized lithography to make gold contacts upon which CNT’s were deposited, creating an electrical connection and allowing for C-AFM measurements. A similar experiment could be carried out with the present experimental setup.
2.4 Conclusions

C-AFM was used to measure the resistivity of single IM7 carbon fibers embedded in a unidirectional laminate. Samples were manufactured to create fully conducting pathways capable of make C-AFM measurements. Basic analyses using the relationship between resistance and resistivity yielded a measurement of IM7 resistivity of $(3.2 \pm 0.8) \times 10^{-3} \ \Omega \cdot \text{cm}$, but that result was higher than the expected manufacturer specification of $1.5 \times 10^{-3} \ \Omega \cdot \text{cm}$. A series of resistance measurements was carried out on fibers of different lengths, and those results were used to determine the presence of 960 $\Omega$ of contact resistance in the experimental setup. Accounting for this contact resistance, the resistivity of IM7 fibers was measured to be $(1.9 \pm 1.1) \times 10^{-3} \ \Omega \cdot \text{cm}$, which agrees with the manufacturer specification. However, while expected for these types of experiments, the uncertainty of this resistivity measurement was large. Implementation of a control experiment with a well-characterized material could further validate this result and its large uncertainty. In all, using C-AFM to measure the resistivity of IM7 carbon fibers was shown to be an appropriate technique when the effect of contact resistance was incorporated into the analysis.
Chapter 3: Conductivity Measurements with sMIM

3.1 Introduction

A novel technique born out of traditional AFM is Scanning Microwave Impedance Microscopy (sMIM). This technique uses a specialized cantilever to transmit a 3 GHz microwave through the tip, impinge the microwave on a material surface, and receive the reflected microwave. Observing the change in the microwave signal yields information about the real and imaginary parts of the signal, which correspond to conductance and capacitance of the material.29

These microwave measurements are made possible by a special, shielded cantilever and tip assembly (PrimeNano Inc.).30 Figure 10 shows an optical microscope and scanning electron microscope (SEM) images of the cantilever.

![Figure 10: Optical and electron microscope images of sMIM AFM tip. (a): Optical microscope image of chip with cantilever. The chip is 1.25 mm in width. (b) SEM image of cantilever. (c): Higher objective SEM image of cantilever. The shielding of the chip and cantilever extends fully up to the tip, which is exposed to transmit and receive microwaves. Images modified from originals provided by Eric Seabron (UIUC).](image)

The contact pad noted in Figure 10a is the point of interaction between the tip and the sMIM tip holder. A coaxial cable delivers the microwave signal from the sMIM electronics to
the AFM head, where the sMIM tip holder interfaces with the contact pad. The microwave signal then travels from the contact pad, through the built in coaxial line on the chip, to the tip. Figure 10b shows an SEM image of the end of the cantilever, and Figure 10c shows a higher magnification image of the end of the cantilever. These images show the shielding wraps around the entire cantilever up to the pyramid-shaped tip that is exposed. The radius of the apex of the tip is nominally 50 nm.

This technique operates in much the same way as traditional AFM. The tip is scanned across the material in a raster-like motion, measuring the topography of the sample. As the tip is tracing along the material surface, the 3 GHz microwave is continuously impinging upon the sample and obtaining microwave information. The reflected microwave information is processed with the sMIM electronics, which relate the amplitude and phase of the reflected microwave to the real and imaginary parts of the complex impedance between the tip and the sample. These real and imaginary parts of the complex impedance are the conductance (or sMIM-R) and capacitance (or sMIM-C) signals, respectively, for the sample.

The sMIM technique is currently a qualitative measure of conductance (or capacitance). Thus, only relative spatial variations in conductance and capacitance are possible. Furthermore, conductance and capacitance are geometry dependent quantities, whereas the ideal output of this technique would be information on conductivity and dielectric constant (permittivity), which are intrinsic material properties. Previous work has shown that there exists an empirical relationship between sMIM capacitance signal (in volts) and permittivity.25 The researchers showed that on a semi-log plot of sMIM capacitance signal vs. log of permittivity, there is a linear relationship between the two quantities. This calibration curve was used to quantify permittivity with sMIM; this work did not address conductivity, though a similar calibration curve could be produced for
conductivity by using materials with various conductivities on multiple orders of magnitude. There has also been work using finite element simulations of the sMIM tip-sample impedance to predict the relationship between sMIM signal and conductivity for a given sample geometry, although with limited accuracy of an order of magnitude.\textsuperscript{31}

In this work conductivity of an IM7 carbon fiber is examined with sMIM. A calibration curve of sMIM conductance signal vs. log of conductivity using doped silicon standards with known conductivities was also examined. Additionally, modeling of the sMIM tip-sample impedance was attempted.

3.2 Materials and Methods

Use of the sMIM system first requires calibration of the signal by scanning a calibration sample. The electronics of the sMIM system decompose the real (conductance) and imaginary (capacitance) parts of the microwave signal and convert them into analog signals, which are displayed through the AFM analog user input channels, called User0 (U0) and User1 (U1). The analog signals output from the sMIM electronics must be calibrated such that only one AFM user input channel contains real (conductance) information and the other contains only imaginary (capacitance) information. This phenomenon is shown graphically in Figure 11 below. Initially, there is an arbitrary phase difference, $\phi$, that separates the real and imaginary parts of the microwave signal from the AFM analog user input channels. This misalignment is due to the imperfect interface between the contact pad and sMIM tip holder. When the position of the contact pad changes relative to the tip holder electronics, the phase difference between the microwave signal and the AFM input channels will also change.
A contact mode area scan was performed on the calibration sample to begin the calibration process. The calibration sample is Alumina dots (Al₂O₃) on a silicon oxide (SiO₂) substrate, and the materials on the calibration sample were chosen by PrimeNano such that there exists only a capacitance difference between the Al₂O₃ dot and the SiO₂ substrate while there is a minimal conductance difference. As a result, scanning these materials should only produce capacitance signal changes moving from the SiO₂ substrate to the Al₂O₃ dot. A phase offset of the sMIM signal, called the demodulation phase, was input and varied until signal contrast was only observed in one channel, effectively negating the initial arbitrary offset, \( \phi \).

Typical height and microwave signals obtained for an area scan of the sample after tuning of the demodulation phase are shown in Figure 12 below. Figure 12 shows that there is only contrast being produced in one channel, with some small remnants of the signal being observed in the other channel. This image indicates that the sMIM signals and AFM channels are aligned. Furthermore, because the sMIM signals and AFM channels can remain aligned for any sMIM
signal rotation of $n \ast \pi / 2$, where $n$ is an arbitrary integer, either U0 or U1 could contain the capacitance information sought during the calibration process (with U0 and/or U1 possibly inverted depending on the angle of rotation). Thus, this calibration process revealed which channels contained the conductance and capacitance sMIM signals and if those signals were inverted.

![Figure 12: Alumina dot calibration sample after demodulation phase tuning. sMIM signal information is only being produced in one channel. This image indicates that channel shows the imaginary part of the signal and shows capacitance information. The other channel shows the real part of the signal, the conductance information, and shows almost no contrast. Provided by Eric Seabron (UIUC)](image)

After the calibration was complete, scanning of desired samples began. All images were collected in contact mode with a 1 Hz scan rate and 0.25 V set point voltage (SP). Large area scans on the order of 20 µm were executed to find suitable scanning areas. When a suitable area was found, NAP (near-as-possible) mode scans (implemented through Asylum software) were performed on the desired location. As discussed in Chapters 1 and 2, traditional AFM performs successive line scans on a material surface to create a 3D image; NAP mode performs a secondary line scan after each standard AFM line scan in the same x-y location but at an height offset, called the delta height, $\Delta h$, from the material surface. This concept is schematically shown in Figure 13 below.
Figure 13: Schematic of NAP mode operation. First, a standard contact mode line scan is performed. After that line scan is completed, a second scan, called the NAP mode scan, is performed. The cantilever follows the same path as the preceding contact mode line scan, but offset by a height above the surface, $\Delta h$. Successive contact mode line scans followed by NAP mode line scans are performed to create the standard contact mode 3D image and an accompanying NAP mode 3D image.

NAP mode was implemented here to eliminate microwave signal and electronics drift with time. Initial contact mode scans revealed significant signal drift in time, noted by a varying signal on homogeneous materials. By moving the tip away from the surface with a large $\Delta h$, between 1 and 5 $\mu$m, the NAP mode image, the 3D image created by the successive secondary scans, measures the signal in air which is effectively the drift in the signal. The NAP mode image can be subtracted from the standard contact mode image to eliminate this drift. This technique for eliminating drift has been implemented in earlier sMIM work as well.\textsuperscript{25}
Scans of carbon fiber laminates and doped silicon were performed under similar scanning conditions. Average values of sMIM signals on the doped silicon were obtained from averaging the sMIM signal of a 20 µm area scan on the doped silicon.

Scans of carbon fiber laminates were performed on the same unidirectional IM7/977-3 laminates with polished cross-sections transverse to the fiber axis (transversely polished) used in the C-AFM experiments. Unidirectional IM7/977-3 laminates with polished cross-sections parallel to the fiber axis (axially polished) were made using the same procedures as outlined in Chapter 2, except they were mounted on a glass slide with cyanoacrylate adhesive instead of silver paint and had no magnet, which are not required for sMIM operation. These axially polished samples were scanned and compared against the transversely polished samples to examine the anisotropy of conductivity of the IM7 fibers.

To create the experimental conductivity calibration curve discussed earlier in this chapter, materials had to be selected to provide calibration standards with various conductivity values on multiple orders of magnitude for scanning with sMIM. Doped silicon was chosen as the target material for this application for several reasons. Silicon is a bulk material that can achieve uniform conductivity both above and below the known conductivity of an IM7 fiber (~500-700 S/cm) through doping. Silicon also provides the ability to control the doping concentration, and thereby control and select the desired conductivity. Practical limits were a concern, however, as the 3 GHz microwave produced by the tip can penetrate up to 100 nm into the material being scanned. Thus, it was necessary that calibration standards have uniform resistivity at least 100 nm deep into the surface of the material to ensure that the microwave was being attenuated by material of only the desired conductivity.
Doped silicon calibration standards were obtained through a combination of purchased, and manufactured wafers. Three P-type, Boron doped silicon wafers were purchased (UniversityWafer), and one undoped silicon on insulator (SOI) wafer was purchased (UniversityWafer) and then doped by Dr. Seung-Kyun Kang (UIUC). The SOI wafer was N-type diffusion doped with solid-phase Phosphorous in an 1100 °C furnace for 10 minutes.

The resistivities of all four wafers were measured with a 4-point probe. A piece of each wafer was measured 10 times at different locations to obtain the average and standard deviation values of resistance. These resistance values were multiplied by a geometric factor determined by the spacing of the four probes to obtain the sheet resistance, and the sheet resistance was multiplied by the thickness of the wafer to obtain the resistivity. In the case of the SOI wafer, the thickness used was the thickness of the top Si layer and not the thickness of the entire wafer. The conductivities (inverse of resistivity) of the three purchased wafers were 1.3 ± 0.2 S/cm, 80 ± 4 S/cm, and 260 ± 6 S/cm, and the conductivity of the SOI wafer was 1842 ± 131 S/cm.

These wafers were also analyzed with Secondary Ion Mass Spectrometry (SIMS) to examine their doping concentrations with depth and ensure their doping depths were greater than 100 nm. An oxygen beam was used for analyzing the P-type wafers, and a cesium beam was used for analyzing the n-type wafer. Doping depth profiles of these wafers are shown in Figure 14.
Figure 14a and b. Figure 14c and d on next page.
Figure 14: Doping depth profiles of doped silicon obtained through SIMS. The red lines denote the concentration of silicon, the purple lines denote the concentration of the Boron, and the blue line denotes the concentration of Phosphorous. (a): Boron doped Si, $\sigma = 1.3 \pm 0.2$ S/cm. (b): Boron doped Si, $\sigma = 80 \pm 4$ S/cm. (c) Boron doped Si, $\sigma = 260 \pm 6$ S/cm. (d): Phosphorous doped SOI, $\sigma = 1842 \pm 131$ S/cm. The downward spikes on the otherwise flat curves are scanning artifacts. Also note that while there appears to be more non-uniformity in (a), the measured variations are the noise of the data, which is more visible in (a) because of the lower dopant concentration on the magnifying log scale.
The downward spikes seen in Figure 14 are scanning artifacts. The purchased P-type wafers were doped completely through their thickness, and the profiles in Figure 14a-c show the dopant concentration does not change appreciably going 1500 nm into the material. While there appear to be significant fluctuations in the doping concentration for the wafer in Figure 14c, these fluctuations are noise and are less visible in higher doping concentration measurements because the y-axis is on a log scale. The SOI wafer doping profile also does not show appreciable change in dopant concentration up to 200 nm, which was the thickness of the top silicon layer.

To create the experimental calibration curve, the doped silicon wafers were scanned using the parameters listed earlier in this section. The sMIM conductance signal for an area scan on each wafer was averaged over the entirety of the area scan to give an average sMIM conductance signal for that wafer’s level of conductivity. This process was done for all wafers examined. Standard deviations of the area scans were also evaluated to characterize uncertainty. Transversely polished IM7/977-3 laminates were scanned to be compared against the calibration curve created by the doped silicon; the average value of the sMIM conductance signal on a fiber was averaged in the same manner as the doped silicon.

A linear regression of the doped silicon data was performed to create a calibration curve of sMIM conductance signal vs. material conductivity. The experimentally obtained sMIM conductance signal for the IM7 fiber was then used to convert to conductivity of the IM7 fiber. The IM7 average conductivity obtained by sMIM was compared against the conductivity experimentally measured with C-AFM to evaluate the accuracy of this quantification method.

The second methodology for quantifying the conductivity of IM7 carbon fibers with sMIM used modeling of the tip-sample complex admittance, $Y$ (inverse of impedance), following
the methodology of [32]. COMSOL software was used to run these finite element simulations carried out by PrimeNano Inc. The permittivities of the epoxy and carbon fiber are needed for these simulations, but their exact values were not known. Best guesses of 4 for the 977-3 epoxy and 10 for the IM7 fiber were used based on literature that cited similar values for epoxies and graphite, respectively.

The finite element simulations calculated the tip-sample admittance between a tip of nominal geometry and the material of interest. Two simulations were executed, one with the material of interest being a semi-infinite plane of epoxy and the other with a semi-infinite plane of carbon fiber. To obtain the admittance of the true geometry of the carbon fiber, the admittance of the semi-infinite plane of epoxy, $Y_{\text{epoxy}}$, was subtracted from the admittance of the semi-infinite plane of carbon fiber, $Y_{\text{IM7}}$, shown in Equation (9).

$$\Delta Y = Y_{\text{IM7}} - Y_{\text{epoxy}} \quad (9)$$

To make an analogous relationship between the modeled admittance and the experimental data, the average sMIM-R signal on the epoxy (sMIM-R$_{\text{epoxy}}$) was subtracted from the average sMIM-R signal on the fiber (sMIM-R$_{\text{IM7}}$). This was similarly done for the sMIM-C information and is shown in Equations (10) and (11).

$$\Delta \text{sMIM-R} = (\text{sMIM} - R_{\text{IM7}}) - (\text{sMIM} - R_{\text{epoxy}}) \quad (10)$$

$$\Delta \text{sMIM-C} = (\text{sMIM} - C_{\text{IM7}}) - (\text{sMIM} - C_{\text{epoxy}}) \quad (11)$$

where $\Delta \text{sMIM-R}$ and $\Delta \text{sMIM-C}$ are the epoxy signal-subtracted quantities.

It was assumed that $\Delta \text{sMIM-R}$ is proportional to Re($\Delta Y$) and $\Delta \text{sMIM-C}$ is proportional to Im($\Delta Y$), and their constants of proportionality are the same. The constant of proportionality cannot be directly known. The ratio of Re($\Delta Y$) to Im($\Delta Y$) was computed and was plotted against
conductivity; it was expected that this analysis would yield a linear relationship between \( \text{Re}(\Delta Y) / \text{Im}(\Delta Y) \). Similarly the ratio of \( \Delta s_{\text{MIM-R}} \) to \( \Delta s_{\text{MIM-C}} \) was evaluated. The aforementioned constants of proportionality are the same, and the following relationship holds true.

\[
\frac{\Delta s_{\text{MIM-R}}}{\Delta s_{\text{MIM-C}}} = \frac{\text{Re}(\Delta Y)}{\text{Im}(\Delta Y)}
\]  

(11)

The \( \Delta s_{\text{MIM-R}}/\Delta s_{\text{MIM-C}} \) ratio can be directly compared against the \( \text{Re}(\Delta Y) / \text{Im}(\Delta Y) \) values predicted for the known conductivity of IM7 carbon fibers to evaluate the accuracy of this quantification method.

### 3.3 Results and Discussion

A sample set of images from a scan on a transversely cross-sectioned carbon fiber sample is shown in Figure 15. Figure 15a shows the height information channel, Figure 15b shows the cantilever deflection information, Figure 15c shows the sMIM conductance channel for the contact mode scan, Figure 15d shows the NAP mode sMIM conductance signal, taken at \( \Delta h = 5 \) \( \mu \text{m} \), Figure 15e shows the subtraction of the NAP image from the contact image, and Figure 15f shows the data from a line scan across the NAP-subtracted image 15e.
Figure 1a-d. Figure 1e and f on next page.
Figure 15: sMIM conductance signal images for transversely polished carbon fiber sample. The diameter of the fibers is 5 µm. (a): Height information. (b): Deflection information (effectively the derivative of height). (c) Contact sMIM conductance signal. (d) NAP sMIM conductance signal. (e) Contact – NAP Image. (f) Line scan along line shown in (e). A Distance of 0 corresponds to the point at the left side of the image. The signal on the epoxy is practically zero after NAP subtraction. All images are retraces.
The signal in the NAP image is quite small compared to the contact image, with the signal in the NAP image on the order of hundreds of mV, while the contact image is on the order of several volts. When the images are subtracted, the effect is not largely noticeable. But observation of the line scan in Figure 15f shows that the NAP subtraction made the signal on the epoxy \(-40\) mV, effectively zero when compared to the signal on the fibers, since the epoxy is insulating and should provide no conductance. The average sMIM conductance signal along the line scan from Figure 15f is \(1.615 \pm 0.918\) V, where the uncertainty comes from the standard deviation of the data.

Figure 15e shows a large variation in the conductance on the center carbon fiber, with the lowest value seen on the carbon fiber at \(-0.069\) V and the highest value observed at \(5.781\) V. The average signal on the carbon fiber is \(1.997\) V with a \(0.593\) V standard deviation.

Figure 16 shows a similar set of images to Figure 15 but with a sample cross-sectioned parallel to the fiber axis. These images were collected under the same conditions as the images in Figure 15, with \(\Delta h = 5\) \(\mu m\).
Figure 16a-d. Figure 16e and f on next page.
Figure 16: sMIM conductance signal images for axially polished carbon fiber sample. Recall that the diameter of the fibers is 5 µm. (a): Height information. (b): Deflection information (effectively the derivative of height). (c) Contact sMIM conductance signal. (d) NAP sMIM conductance signal. (e) Contact – NAP Image. (f) Line scan along line shown in (e). A Distance of 0 corresponds to the point at the left side of the image. The signal on the epoxy is practically zero after NAP subtraction. The single, high value of 6.07 V is likely a scanning artifact. All images are retraces.
Once again, the signal in the NAP image is quite small compared to the contact image, with the signal in the NAP image on the order of tens of mV, while the contact image is on the order of one volt. When the images are subtracted, the effect is not largely noticeable. The line scan in Figure 16f shows that the NAP subtraction has made the signal on the epoxy ~ -60 mV, which is close to zero but not as close as the transversely cross-sectioned samples. The average sMIM conductance signal along the line scan from Figure 16f is $0.504 \pm 0.752$ V, where the uncertainty comes from the standard deviation of the data.

The lines of blue on the right sides of the left and middle fibers seen in Figure 16e are likely scanning and topology artifacts. It is common to see anomalous signal measurements when there are abrupt changes in height on a sample, and because these images are retraces, i.e. the cantilever is scanning from right to left, high signal measurements appear on the right edges of the fibers. The deflection image in Figure 16b shows that there are some scratches on the fibers that seem to correlate with measurements of higher conductance, particularly on the left and center fibers, but also present to a lesser extent on the right fiber. The blue streaks across the fibers also appear to be scanning artifacts, but they do not correspond to any topography on the fibers. Further investigation is required to fully understand what variations in conductance are artifacts and what are real.

The right fiber was examined and found to have an average sMIM conductance signal of 357 mV with a standard deviation of 307 mV. The maximum value on the fiber is 3.968 V while the minimum value on the fiber was -0.052 V. The low standard deviation accompanied by the high maximum value seems to indicate the maximum value is anomalously high and is possibly a scanning artifact.
The average value of the sMIM conductance signal on the transversely cross-sectioned fibers, 1.997 ± 0.593 V, is significantly higher than the 0.357 ± 0.307 V sMIM conductance signal on the axially cross-sectioned fibers. This result is logical, as the conductivity of a carbon fiber is much higher along its fiber axis than across it. It is harder for electrons to move between the basal planes of the turbostratic graphite crystals than it is for electrons to move in the axial direction along the basal planes. Although these results are not strictly quantitative, they provide an estimate of a 5.5 factor of difference between the axial and transverse conductivities. Additional study is required to determine if the true axial and transverse conductivities are being probed here.

Images from scanning of the doped silicon wafers are shown in Figure 17. Figure 17a-d shows images from the $\sigma = 1.3 \pm 0.2$ S/cm silicon, 17e-h shows the $\sigma = 80 \pm 4$ S/cm silicon, and 17i-l shows the $\sigma = 260 \pm 6$ S/cm silicon. The first images are the height information, the second images are the contact sMIM conductance signal, the third images are the NAP conductance signal, and the fourth images are the NAP-subtracted conductance images.
Figure 1a-d. Figure 1e-h on next page.
Figure 17e-h. Figure 17i-l on next page.
Figure 17: Doped silicon height information (Flatten Order 0), contact sMIM conductance signal, NAP sMIM conductance signal, contact – NAP signal for (a)-(d): $\sigma = 1.3 \pm 0.2$ S/cm, (e)-(h): $\sigma = 80 \pm 4$ S/cm, (i)-(l): $\sigma = 260 \pm 6$ S/cm. All images are retraces.

The NAP-subtracted signals were averaged over the 20 $\mu$m area scans to obtain average sMIM signals for each doped silicon conductivity level.

Using these average values, along with the average fiber sMIM conductance signal value on the transverse cross-section sample, a plot of sMIM signal vs. log of conductivity was produced and is shown in Figure 18.
Figure 18: sMIM conductance signal vs. conductivity with doped silicon calibration curve and predicted and measured conductivities of IM7 carbon fiber.

The blue diamonds show the average values of conductivity and sMIM signal for the doped silicon. Error bars have been plotted on this data, but the data markers obscure them. The line is the linear regression of the doped silicon data. The red square is the average sMIM conductance signal on a carbon fiber and the average conductivity value of the IM7 carbon fiber measured by C-AFM, $\sigma_{\text{measured}} = 526 \pm 304$ S/cm. The blue square is the average sMIM conductance signal on a carbon fiber and the predicted conductivity from the doped silicon linear regression, $\sigma_{\text{predicted}} = 2261 \pm 732$ S/cm. All error bars are the standard deviations of their respective values. This plot shows the measured conductivity of the IM7 carbon fiber does not
agree with the predicted conductivity value from the doped silicon calibration. The measured and predicted quantities are off by a factor of 4.3.

The immediate reason for this discrepancy between theory and experiment is illustrated through Figure 19, which shows only the sMIM signal vs. log of conductivity data for the doped silicon.

![Figure 19: sMIM conductance signal vs. conductivity for doped silicon only. There is a lack of a clear, linear trend between conductivity and sMIM signal for these doped silicon calibration standards.](image)

Figure 19 shows there is no clear trend in the doped silicon data with respect to conductivity. The $R^2$ value of the linear regression is 0.087, which is extremely poor.

Furthermore, the sMIM signal for the doped silicon data is negative while the IM7 data is positive. It is common for data to be inverted and produce negative values as discussed earlier in Section 3.2; the sMIM-R and sMIM-C signals can remain aligned for any sMIM signal rotation of $n \pi / 2$, where $n$ is an arbitrary integer. Thus, either AFM information channel could contain either the sMIM-R and sMIM-C signals, with the AFM information channels possibly inverted.
depending on the angle of rotation. However, it is uncharacteristic for the signal to be negative with one sample but be positive with another.

One possible reason for this discrepancy is due to the native oxide layer that naturally forms on silicon. A native oxide forms on the surface of any silicon wafer, and this can alter the electrical measurements from sMIM. The sMIM microwave is attenuated by both the doped silicon and the oxide layer. As a result, the measurements done on an IM7 fiber, that does not form an oxide, and doped silicon, which does form an oxide, are different and cannot be directly compared. Different thicknesses of oxide layers could form on different silicon wafers, changing the sMIM measurement between these like materials. Thus, the comparison amongst different doped silicon wafers and between the doped silicon and IM7 fiber may be ill posed.

The second potential root cause of the lack of correlation may be due to the presence of the depletion layer in the silicon. When electromagnetic radiation interacts with a semiconductor, it pushes the carriers (charges) within the semiconductor away from the impinging radiation. The region that has been evacuated by carriers is called the depletion layer. This depleted silicon will not attenuate the microwave in the same manner as if there were no carrier depletion. Thus, the sMIM conductance signal obtained here may not be measuring the macroscopic conductivity of the doped silicon, limiting the efficacy of this experimental calibration curve quantification strategy.

With one method for quantification having not succeeded, the other method utilizing computational methods was attempted. Figure 20 shows the contact sMIM capacitance signal, NAP capacitance signal, and NAP-subtracted capacitance image for the same transverse cross-section shown in Figure 15. This data was used to calculate the necessary ΔsMIM-C data as detailed in Section 3.2.
Figure 20: sMIM capacitance signal images for transversely polished carbon fiber sample. Recall that the diameter of the fibers is 5 µm. (a): Contact sMIM capacitance signal. (b): NAP capacitance signal. (c): Contact – NAP sMIM capacitance image. All images are retraces.
The average sMIM capacitance signal on the central fiber was -672 mV with a standard deviation of 85 mV. The average value is negative because the channel was inverted during the calibration process.

Figure 21 shows the plot of $\text{Re}(\Delta Y)/\text{Im}(\Delta Y)$ vs. conductivity that was obtained from the computational simulations performed by PrimeNano Inc.

Figure 21: Modeled $\text{Re}(\Delta Y)/\text{Im}(\Delta Y)$ vs. conductivity plot with predicted IM7 result and measured IM7 $\Delta$sMIM-R/$\Delta$sMIM-C data, original and inverted (multiplied by -1 to account for inversion of sMIM-C signal). Modified original provided by PrimeNano, Inc.
The modeled result for the relationship between \( \text{Re}(\Delta Y)/\text{Im}(\Delta Y) \) vs. conductivity is shown with a black line. The simulations computed a linear relationship between \( \text{Re}(\Delta Y)/\text{Im}(\Delta Y) \) and conductivity. The model predicted an admittance ratio for the conductivity of an IM7 fiber to be \( 30 \pm 17 \), plotted as a red square. The uncertainty of the predicted IM7 result is quite large because of the large uncertainty of the measured IM7 conductivity with C-AFM. The \( \Delta s_{\text{MIM-R}}/\Delta s_{\text{MIM-C}} \) ratio of the IM7 fiber was calculated to be \( -6.4 \pm 2.2 \) and is plotted as an orange square. Equation (11) states the admittance and sMIM signal ratios are equal, and thus they can be plotted together. Multiplying the capacitance signal by -1 to obtain a \( \Delta s_{\text{MIM-R}}/\Delta s_{\text{MIM-C}} \) ratio of \( 6.4 \pm 2.2 \) corrects the inversion; this data point is plotted as a blue square. The predicted result is off from the inverted experimental data by a factor of 4.7.

The first potential reason for the lack of agreement is the incorrect permittivities used as inputs for the model. Dielectric constants can be well characterized for epoxies, but the necessary experiments for characterizing 977-3 were not feasible within the timeframe and scope of this work. Data for 977-3 has not been published to this author’s knowledge. Permittivity characterization techniques require bulk materials, making the carbon fibers ill suited for evaluation. Experiments could be performed on a bulk carbon fiber/epoxy laminate, but additional analysis, such as the use of effective medium theory, would be required to calculate the permittivity of the carbon fiber.

The second potential reason for this disagreement is due to the differences in the NAP image for the conductance and capacitance channels. While the conductance NAP image shows extremely little if any signal from the carbon fiber in Figure 5d, the capacitance NAP image in 20b shows a small outline of the fiber, indicating NAP scan contains signal produced by carbon fiber instead of just the surrounding air. Thus, when the NAP subtraction occurs, the resulting
image has had some true signal from the carbon fiber taken out. These remnant features of the fiber in the NAP image are small compared to the overall signal, but may be significant when calculating the $\Delta s_{\text{MIM-R}}/\Delta s_{\text{MIM-C}}$ ratio.

### 3.4 Conclusions

sMIM was used to examine the spatial variations of conductivity on IM7 carbon fibers. Experiments qualitatively showed large variations in conductance on the transverse cross-section of the carbon fiber. Axial cross-section samples showed markedly lower measured conductance values than the transverse cross-section samples, a result that agrees with the understanding of the morphological structure of carbon fibers. The experimental procedure for quantifying sMIM conductivity measurements was not successful. Differences in measurements on semiconducting and conducting materials make this experimental strategy for quantification not presently feasible. Similarly, computational efforts to create a calibration curve were not entirely successful, but showed some promise. The predicted admittance ratio for the IM7 fiber was a factor of 4.7 off from the measured value; however, this methodology shows some potential for future application if material property inputs into the model can be refined and experimental protocols can be enhanced to achieve better isolation of system drift from the desired sMIM signals.
Chapter 4: Conclusions and Future Work

The conductivity of IM7 carbon fibers was investigated using C-AFM and sMIM. C-AFM experiments were carried out on IM7/977-3 unidirectional laminates. These experiments measured the resistivity of the IM7 fibers, but this result was higher than the expected manufacturer specification. A series of experiments using IM7 fibers of different lengths showed the presence of contact resistance in the experimental setup. By accounting for this contact resistance, the resistivity of IM7 fibers was accurately measured.

The uncertainty associated with the resistivity of IM7 fibers is large, but implementation of a control experiment with a micro- or nano-scale material of well-known conductivity, such as a metal like gold or silver, would lend strong support to the experiments done in this work. Dai et al. laid the groundwork for doing C-AFM with CNT’s\textsuperscript{19}, and that work could be translated here to metallic nanowires to verify the measurements and uncertainty of the conductivity of carbon fibers measured in this work.

sMIM was used to examine the local, spatial variations in conductivity on IM7 carbon fibers. Experiments revealed large variations in conductance on transverse fiber cross-sections. Axial fiber cross-sections showed markedly lower conductance values compared to transverse cross-sections, which agrees with the morphological understanding of carbon fibers. Efforts at quantification of sMIM conductivity measurements were not successful with either experimental or computational approaches. These methodologies were not fruitless, but rather need improvements to show more promise.

The experimental calibration curve method was limited by the choice of materials available to use as conductivity standards. Doped semiconductors were one of the few choices possible to manufacture materials with the desired conductivities, but the presence of both the
native oxide and depletion layers make semiconductors not currently usable for this application. Future work may be possible with semiconductors if more is known about the exact details of the native oxide and depletion layers and some strategy is formulated to account for them.

Similar to the experimental method, the computational methodology for quantifying conductivity measurements was limited by a lack of material information. Obtaining the permittivity of 977-3 would be tedious but possible work. Measuring the permittivity of IM7 fibers would be difficult and require more intensive study. This computational method, though, with the right material inputs and tweaking of the NAP subtraction methodology, has some potential to deliver on the idea of quantification of sMIM.
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