Nano-scale RF/Microwave Characterization of Materials' Electromagnetic Properties

Joshua Allen Myers
Wright State University

Follow this and additional works at: http://corescholar.libraries.wright.edu/etd_all

Part of the Electrical and Computer Engineering Commons

Repository Citation
Nano-scale RF/Microwave characterization of materials' electromagnetic properties

A thesis submitted in partial fulfillment of the Requirements for the degree of Master of Science in Engineering

By

JOSHUA ALLEN MYERS
B.S.E.P., Wright State University, 2008

2012
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PRESENTED UNDER MY SUPERVISION BY Joshua Allen Myers ENTITLED Nano-scale RF/Microwave characterization of material’s electromagnetic properties BE ACCEPTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering.

____________________________________
Yan Zhuang, Ph.D.
Thesis Director

____________________________________
Kefu Xue, Ph.D., Chair
Department of Electrical Engineering

Committee on Final Examination

____________________________________
Yan Zhuang, Ph.D.

____________________________________
Douglas Petkie, Ph.D.

____________________________________
Robert C. Fitch, Jr., Ph.D.

____________________________________
Andrew Hsu, Ph.D.
Dean, School of Graduate Studies
ABSTRACT


There are two words that describe the direction of today’s electronic technology, smaller and faster. With the ever decreeing size scientists and engineers must have a way to characterize materials in the nm range. In this thesis characterization of nano-materials is discussed based on scanning probe microscopy and an in-depth look at RF/microwave frequencies by scanning microwave microscopy. Recently, low-temperature spin-sprayed ferrite films (Fe3O4) with a high self-biased magnetic anisotropy field have been reported, showing FMR frequency>5 GHz. Such films hold great potential for RF/microwave devices and find immediate applications. In this study, we performed in situ scanning microwave microscopy (SMM) characterization at frequencies between 2.0 GHz and 8.0 GHz. The grain boundary appeared to be more conductive, which might be caused by charge accumulation in the grain boundary space-charge region.
Table of Contents

Chapter 1: Introduction to Scanning Probe Characterization Techniques ........................................ 1

1.1 Scanning Tunneling Microscopy (STM) ................................................................. 2
1.2 Atomic Force Microscopy (AFM) ................................................................. 6
1.3 Scanning Capacitance Microscopy (SCM) ......................................................... 9
1.4 Near-Field Scanning Optical Microscopy (NSOM) .............................................. 11
1.5 Scanning Microwave Microscopy (SMM) ......................................................... 12
1.6 Summary .......................................................................................................... 15
1.7 References ......................................................................................................... 16

Chapter 2: Magnetic dynamics of ferromagnetic materials and SMM set-up .................. 20

2.1 Introduction ....................................................................................................... 20
2.2 Electromagnetic Properties ............................................................................. 20
2.3 Magnetic dynamics ............................................................................................ 24
2.4 Magnetic Permeability at RF/microwave Frequencies ....................................... 26
2.5 Scanning Microwave Microscopy Set-up .......................................................... 29
2.6 References ......................................................................................................... 36

Chapter 3: Experimental Results and Discussions ..................................................... 38

3.1 Introduction ....................................................................................................... 38
3.2 Experiments ..................................................................................................... 40
3.3 Results and Discussions .................................................................................. 41
3.4 References ......................................................................................................... 51

Chapter 4: Conclusion ................................................................................................. 54

4.1 Various Experimental Results ........................................................................... 54
4.2 Future Works ..................................................................................................... 60
4.3 References ......................................................................................................... 63

Publications ............................................................................................................... 64
Appendix A ................................................................................................................ 65
Appendix B ................................................................................................................ 93
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1: Xenon atoms on a single-crystal nickel surface</td>
<td>2</td>
</tr>
<tr>
<td>1.2: Individual iron atoms on a copper surface positioned as a circular corral</td>
<td>2</td>
</tr>
<tr>
<td>1.3a: Classical barrier</td>
<td>3</td>
</tr>
<tr>
<td>1.3b: Quantum barrier</td>
<td>3</td>
</tr>
<tr>
<td>1.4: STM tip sample interaction</td>
<td>4</td>
</tr>
<tr>
<td>1.5: STM raster scanning and tip sample interaction</td>
<td>5</td>
</tr>
<tr>
<td>1.6: Forces between AFM tip and sample</td>
<td>6</td>
</tr>
<tr>
<td>1.7: Contact mode AFM</td>
<td>7</td>
</tr>
<tr>
<td>1.8: SCM tip diagram</td>
<td>10</td>
</tr>
<tr>
<td>1.9: NSOM tip sample interaction</td>
<td>12</td>
</tr>
<tr>
<td>1.10: SMM probe tip shown with 50 Ohm shunt resistor</td>
<td>14</td>
</tr>
<tr>
<td>2.1: Electron orbiting Nucleus and Electron spin</td>
<td>20</td>
</tr>
<tr>
<td>2.2: Electron spin paring in paramagnetic material</td>
<td>21</td>
</tr>
<tr>
<td>2.3: Bloch Wall</td>
<td>22</td>
</tr>
<tr>
<td>2.4: Neel Wall</td>
<td>23</td>
</tr>
<tr>
<td>2.5: Hysteresis loop in a ferromagnetic material</td>
<td>24</td>
</tr>
</tbody>
</table>
2.6: Landau-Lifshitz-Gilber equation model of a spinning electron .......... 26
2.7a: Complex permeability vs. Frequency ................................................. 27
2.7b: Complex permeability vs. Frequency .................................................. 27
2.7c: Complex permeability vs. Frequency .................................................. 28
2.7d: Complex permeability vs. Frequency .................................................. 28
2.7e: Complex permeability vs. Frequency .................................................. 28
2.8: Agilent 5420 AFM connected to an Agilent PNA 5230C
                               to form a SMM system .................................................... 30
2.9: AFM 5420 in isolated box ................................................................. 30
2.10: Normal AFM Assembly ................................................................. 31
2.11: Scanning Microwave Microscope Assembly .................................... 31
2.12: SMM System ............................................................................... 31
2.13: Diagram of SMM tip ........................................................................ 32
2.14: SMM Tip ....................................................................................... 33
2.15: PNA to SMM Probe Diagram ........................................................ 34
2.16: Amplitude vs. Frequency and Phase vs. Frequency
                               plot of SMM tip in air from 1.9 to 40 GHz .......... 35
2.17: Frequency scan of the SMM tip in air from 20.75845 GHz to
                               2.076685 GHz ................................................................. 36
3.1: Simulated and Measured complex permeability spectra ..................... 42
3.2a: Topography of multilayer at \( \lambda/2 \) ..................................................... 44
3.2b: Amplitude of multilayer at \( \lambda/2 \) ............................................. 44
3.2d: Topography of multilayer at $\lambda/4$ ................................................................. 44
3.2e: Amplitude of multilayer at $\lambda/4$ ................................................................. 44
3.2c: Phase of multilayer at $\lambda/2$ ................................................................. 44
3.2f: Phase of multilayer at $\lambda/4$ ................................................................. 44
3.3: Model of the SMM circuit with $Z_L$ as the sample ......................................... 46
3.4: MatLab simulation of equation 3.3 for both $\lambda/2$ and $\lambda/4$ frequencies ....... 49
3.5a: Surface morphology of multilayer ................................................................. 50
3.5b: Amplitude of the reflection coefficient .......................................................... 50
3.5c: Surface morphology of the graphene oxide/Pt sample .................................. 50
3.5d: Amplitude of the reflection coefficient of the graphene oxide/Pt sample .......... 50
4.1a: HOPG at $\lambda/4$ topography ......................................................................... 55
4.1b: HOPG at $\lambda/4$ s$_{11}$ amplitude ................................................................. 56
4.1c: HOPG at $\lambda/4$ s$_{11}$ phase ................................................................. 56
4.2a: HOPG topography cross section view ............................................................ 57
4.2b: HOPG s$_{11}$ amplitude cross section view .................................................... 57
4.2c: HOPG s$_{11}$ phase cross section view ............................................................ 57
4.3a: HOPG at $\lambda/2$ topography ......................................................................... 58
4.3b: HOPG at $\lambda/2$ amplitude ......................................................................... 58
4.3c: HOPG at $\lambda/2$ phase ......................................................................... 59
4.4a: HOPG topography cross section view ............................................................ 59
4.4b: HOPG s$_{11}$ amplitude cross section view .................................................... 59
4.4c: HOPG $s_{11}$ phase cross section view .............................................................. 60
4.5: Error flow graph of one-port $S_{11}$ measurement ........................................... 60
4.6: Sketch of CASUB (a) cross-sectional view, and (b) top-view ......................... 61
LIST OF TABLES

1.1: Various modes of AFM ................................................................. 8

3.1: Summary of film structural and magnetic properties ......................... 42
Chapter 1: Introduction to Scanning Probe Characterization Techniques

Nano-scale materials have become a large area of interest in the past few years. The characterization of these materials has allowed them to be incorporated into many different applications such as entertainment systems [1], computers [2], vehicles [3], and even clothing [4]. The characterization of these materials can be accomplished by many different ways including Scanning Electron Microscopy (SEM) [5], Transmission Electron Microscopy (TEM) [6], and Scanning Probe Microscopy (SPM) [7]. Out of these methods SPM shows the most potential by being able to measure a large range of properties in a non-destructive manner with great accuracy and resolution. SPM includes Scanning Tunneling Microscopy (STM) [8], Atomic Force Microscopy (SFM) [9], Scanning Capacitance Microscopy (SCM) [10], Scanning Microwave Microscopy (SMM) [11], and many others. In this work we will mainly focus on SMM because of its ability to extract the topography and electromagnetic properties of the sample simultaneously.
1.1 Scanning Tunneling Microscopy (STM)

Introduction:

STM was the precursor to Atomic Force Microscopy (AFM). STM was invented by Gerd Binnig and Heinrich Rohrer at IBM Research – Zurich [8]. G Binning and H. Rohrer won the Nobel Prize in Physics in 1986 for their design of the scanning tunneling microscope. Since then, there are tremendous work reported by using STM, such as using a STM to move individual xenon atoms on a single-crystal nickel surface to form the famous image in figure 1.1 [12].

Also in figure 1.2 individual iron atoms were positioned in a circular closed form (corrals) on a copper (111) surface with a STM to produce this image. This image shows that there are a series of discrete resonances inside of the corral [13].

| Figure 1.1: Xenon atoms on a single-crystal nickel surface | Figure 1.2: Individual iron atoms on a copper surface positioned as a circular corral. |
Principle:

Figure 1.3a shows the classical physics barrier. When an electrical barrier separates two conductors, electrons cannot move from one conductor to the other unless the electron has enough energy to go over the barrier. Figure 1.3b is the quantum physics approach. In this figure, due to the Heisenberg uncertainty principal, electrons have a finite probability of tunneling through the barrier.

In STM the media between the tip and sample, usually a vacuum is the barrier. A voltage is placed across the tip and the sample and if the tip is close enough to the sample a tunneling current is induced. In early analysis of tunneling current it was found that the one dimensional solution for tunneling current "I" acted in the following manner

\[ I \propto e^{-2\kappa d} \]  

(1.1)

where \(d\) is the distance between each electrode and \(\kappa\) is the decay constant.
\[ \kappa = \frac{\hbar}{\sqrt{2m\phi}} \]  

(1.2)

where \( \phi \) is the effective local work constant defined by the material of the tip and \( m \) is the mass of the electron. From equation 1.1 it can be seen that, since \( \kappa \) is a constant, the distance between the tip and sample controls the tunneling current and that as the width of the barrier increases the tunneling current decreases exponentially.

Figure 1.4 shows the tip and sample on an atomic level. In this figure it shows that 90\% of the tunneling current comes through the tip atom. This is due to the fact that as the distance between the tip and the sample increases, the tunneling current decreases exponentially. It was found that for a change in distance of 1Å the tunneling current increases by an order of magnitude [16]. Since the atoms on a STM tip are around 100Å the atom that is the closest to the sample accounts for most of the tunneling current. Because of this tremendous sensitivity, STM is the only SPM technology that is able to achieve true atomic resolution.

Figure 1.4: STM tip sample interaction. [15]
**Technique:**

Figure 1.5 shows how the tip is scanned across the sample in STM. There are two methods for scanning the tip across the sample, constant height and constant current. In constant height mode the tip remains at a constant height and the current changes as the distance between the tip and the sample changes. Using this method the z axis provides a measurement of the change in current. In constant current mode, as the tip is scanned across the sample the height of the tip is adjusted to maintain a constant tunneling current. In this method the z axis provides a measurement of how much the tip moves [16]. This being said there are several limits to using STM. STM can only measure the topography of a conducting or semiconducting sample since it needs to have two electrodes (the tip and the sample surface). STM is also very sensitive to the change in conductivity over the sample. If the conductivity changes from location to location it makes extracting the topography measurement from the tunneling current very difficult. One other drawback to STM is its sensitivity to environmental changes. Most STM measurements are done in high vacuums to limit the environmental effects.
1.2 Atomic Force Microscopy (AFM)

**Introduction:**

Atomic Force Microscopy was invented by G. Binning, C. F. Quate and Ch. Gerber in 1986 [9]. The AFM was developed to compensate for the limitations of the STM. The basic principle of AFM is to measure different forces that interact between the tip and the sample. For example measuring magnetic force using the Magnetic Force Microscope (MFM) or electrostatic force using the Electrostatic Force Microscope (EMF). Unlike STM, AFM is able to measure many different materials including materials that are non-conducting. While STM is only able to measure the tunneling current AFM is able to measure many different forces that act between the tip and the sample. There are many applications for AFM such as biological sample imaging [18] and nano-material characterization [19].

**Principle:**

![Figure 1.6: Forces between AFM tip and sample][20]
Figure 1.6 shows the interaction forces between the tip of the AFM and the sample. The blue line shows the repulsive force between the tip called the Fermi repulsion force or contact force due to overlapping electron clouds (3). This force dominates in the region of a few Å and is on the order of $3 \times 10^{-3} \text{Nm}^{-1}$. The green line in figure 1.6 shows the attractive force. At this distance the tip is attracted to the sample by van der Waals force. The red line is the combined force vs. distance curve that the tip sees.

These forces are measured by the vertical movement of a cantilever that has the tip attached to it as shown in figure 1.7. This figure shows that as the tip scans across the surface of the sample, these forces act upon the tip causing the cantilever to bend. A laser is reflected off of the back side of the cantilever to a photo detector and the force is then calculated by measured how much the cantilever has moved.

The force that is enacted upon the cantilever follows this equation

$$F = \Delta z k$$

(1.3)

where $\Delta z$ is the distance that the cantilever deflects from equilibrium and $k$ is the force constant. Unlike STM the force enacted upon the tip of the AFM by the sample
is averaged across the atoms in the tip. Because of this the AFM is not able to obtain atomic resolution and is limited to the width of the tip, around 15-20 nm.

**Technique:**

There are several different modes of AFM that have been developed to accomplish this task.

<p>| Table 1.1: Various modes of AFM |</p>
<table>
<thead>
<tr>
<th>Mode</th>
<th>Measurement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic Force Microscopy (EFM)</td>
<td>Electrostatic Charge Density</td>
<td>[22]</td>
</tr>
<tr>
<td>Scanning Capacitance Microscopy (SCM)</td>
<td>Capacitance</td>
<td>[10]</td>
</tr>
<tr>
<td>Tapping Mode AFM</td>
<td>Attractive Force</td>
<td>[23]</td>
</tr>
</tbody>
</table>

In contact mode AFM the tip is kept in hard contact with the sample where the repulsion force is dominant. In contact mode the topography of the sample is able to be obtained. There are two ways to obtain this measurement. Constant force mode and variable force mode (6). In constant force mode the tip deflection is picked up
by a laser reflecting off of the cantilever and then a piezoelectric crystal adjusts the vertical distance of the tip to maintain a constant force between the tip and the surface of the sample. In variable force mode the cantilever is held at a constant height as it is scanned across the surface of the sample and the force depends on the spring constant in the cantilever. Because the tip is in constant contact with the surface of the sample this is the method that we will use for Scanning Microwave Microscopy (SMM), which we will discuss later. Table 1.1 has a list of several other prominent modes of AFM.

1.3 Scanning Capacitance Microscopy (SCM)

Introduction:
SCM was introduced by J. R. Matey and J. Bianc in 1984. The first purpose of SCM was to create a better way to maintain the distance between the tip and the sample in STM. However, in recent years SCM has been used to obtain capacitance information about materials such as doping profiles in semiconducting applications.

Principle:
In SCM the tip of the AFM is scanned over the surface of the sample in non-contact or contact mode. At the same time a potential difference is made between the tip and the sample. The potential is created by an AC voltage between the tip and the surface. The tip acts as one electrode and the sample is the other electrode much like STM [10]. Using this method a parallel plate capacitor is created using both the tip and the sample. The dielectric of the capacitor can be either air (non-contact mode) or some other material (contact mode) such as SiO₂ in silicon technology.
This creates a metal-insulator-substrate capacitor. As with a capacitor the voltage difference between the tip and the sample create charges that gather on the tip. As the voltage changes (AC) the charge on the tip changes. This change is then measured from point to point on the sample as the tip is scanned across.

**Technique:**

In SCM the potential between the tip and the substrate is modulated between 10kHz – 100kHz. One drawback to SCM is, to get an accurate measurement of the capacitance of a sample, the distance between the tip and sample must be constant. Another drawback is that SCM can only measure the capacitance of a sample. SCM is also affected by parasitic capacitances. One of the main sources of parasitic capacitances in SCM is the capacitance between the sample and the cantilever [26]. Because SCM uses the model of a parallel plate capacitor, any other capacitances that are developed due to the setup add to the error in the measurement. Also the strength of the tip to sample capacitance is very difficult to calibrate. Calibration of SCM and sample preparation are critical for the quantification of the results. In SCM a very flat and a uniform, high quality oxide is required of the sample to produce repeatable and quantified results. Even with a well calibrated system only the real part of the dielectric constant (capacitance) can be extracted. The conductivity of the sample is still unknown.
1.4 Near-Field Scanning Optical Microscopy (NSOM)

**Introduction:**

NSOM was introduced by Dürrig, U.; Pohl, D. W.; Rohner in 1986. NSOM is used to view optical images of materials with resolution smaller than half of a wavelength. NSOM is mainly used in the medical field to image biological materials [27]. Extensive research has gone into NSOM in the medical industry since it still maintains the ability to view the optical contrast of conventional microscopy but has the nanometer special resolution of the AFM [28].

**Principle:**

In general the resolution of an optical microscope is dependant of the wavelength. This is described by Abbe’s diffraction limit. Abbe’s diffraction limit states that the resolution that can be obtained optically is limited to about half of the wavelength reflected off of the sample. This is defined by the equation

\[
d = \frac{\lambda}{2(n \sin \theta)}
\]  

(1.4)

where \( \lambda \) is the wavelength, \( n \) is the index of refraction, and \( \theta \) is the angle of incidence. And the resolution is defined by

\[
R = \frac{0.61 \lambda}{n \sin(\theta)}
\]  

(1.5)

where \( \lambda \) is the wavelength and \( n \sin(\theta) \) is called the numerical aperture and is around half of the wavelength.
NSOM broke through this barrier by utilizing evanescent waves [29]. There are two types of waves in the electromagnetic spectrum. The first is the far-field wave. This wave is what is used for classical optics. The near-field wave (evanescent wave) is what is used in NSOM. The evanescent wave is an exponentially decaying wave that is very close to the surface of the sample.

**Technique:**

In NSOM a tip is hovered very close to the surface of a sample to be measured (around 20 to 50 nm). A light is reflected off the sample surface, usually a laser and the near-field reflected light is sensed by a small hole (<\(\lambda\)) in the end of the probe tip. NSOM measures the reflected light intensity to extract the topography of the sample and no electrical or magnetic properties are able to be extracted.

### 1.5 Scanning Microwave Microscopy (SMM)

**Introduction:**

SMM uses the principal of contact mode AFM and connects a performance network analyzer (PNA) to the tip in order to measure the reflection coefficient. There are several works reported in SMM. In the first work an investigation was done into using SMM to measure the doped properties of silicon instead of using SCM. Traditionally, SCM is used to measure the doping levels in silicon. With SMM
however the $S_{11}$ parameter is measured and then converted into capacitance. The conclusion was that the SMM could be used to measure doping profiles in silicon and that the two main parameters that must be considered are the tip voltage and the frequency [30].

In the second work SMM was looked at to perform capacitance measurements on self assembled monolayers by calibrating the SMM using a NIST capacitance standard. The NIST standard is various sized gold pads on a SiO$_2$ layer on a heavily doped silicon substrate. It was shown that the calibration of the SMM capacitance measurements could be reduced to attofarads [31]. Both of these papers demonstrate the ability to obtain some quantitative results using the SMM.

**Principle:**

In SMM a Performance Network Analyzer (PNA) is connected to the tip of the AFM that is being operated in contact mode. The PNA sends a signal in the GHz range to the sample through the tip of the AFM and then compares the reflected signal to the transmitted signal to obtain the magnitude and phase of the reflected signal. The tip is used as a waveguide and the reflection coefficient $\Gamma$ ($S_{11}$ scattering parameter) and topography are measured as the tip scans across the sample surface. The tip also has a shunted 50Ω resistor (figure 1.10). This resistor brings the impedance of the sample much closer to the impedance of the PNA which allows the PNA to have a much higher sensitivity.
Technique:

Using this method the reflection coefficient is separated from the topography of the sample since $\Gamma$ is a direct measurement from the PNA. $S_{11}$ is defined as $\frac{\text{reflected signal}}{\text{incident signal}}$.

$S_{11}$ depends on both the dielectric and magnetic properties of the sample. The dielectric constant of a material is a complex variable, $\varepsilon = \varepsilon' + j\varepsilon''$, where $\varepsilon'$ is the dielectric constant and $\varepsilon'' = \frac{\sigma}{j\omega}$. In this case $\sigma$ is the conductivity of the sample and $\omega$ is the angular frequency. With SMM both the capacitance and the conductivity of a sample can be measured. The $S_{11}$ parameter can be modeled as follows

$$S_{11} = \frac{Z_L - Z_S}{Z_L + Z_S}$$

(1.6)

where $Z_L$ is the impedance of the load and $Z_S$ is the impedance of the source (related to the PNA). Using the complex properties of the impedance this goes to
\[ S_{11} = \Gamma = -\frac{Z_0 + jZ_L \tan(\beta l_0)}{(Z_0 + 2Z_L) + j(2Z_0 + Z_L) \tan(\beta l_0)} \]  

(1.7)

where 
\[ Z_L = \frac{1}{\frac{1}{R} + j \omega C} \]  

(1.8)

\[ Z_0 = 50\Omega, \beta \text{ is the wave number, } l_0 \text{ is the length of the transmission line, } R \text{ is the resistance of the sample, } C \text{ is the capacitance of the sample, and } \omega \text{ is the angular frequency.} \]

**1.6 Summary**

Chapter 2 gives an overview of the properties of electro-magnetic materials and gives the results of simulations of both the Fe\(_3\)O\(_4\)/Photoresist/Fe\(_3\)O\(_4\) multilayer and the equations that are derived in chapter 2 for the complex permeability.

Chapter 3 gives a detailed overview of the SMM setup that was used in the measurements and the results of SMM imaging of the Fe\(_3\)O\(_4\)/Photoresist/Fe\(_3\)O\(_4\) multilayer.

Chapter 4 brings the general conclusion of this these and discusses future uses and techniques of nano-material characterization.
1.7 References


064315-064315-7, 15 September 2010.


Chapter 2: Magnetic dynamics of ferromagnetic materials and SMM set-up

2.1 Introduction

Metallic ferromagnetic (FM) thin films are a prospect for integrated radio frequency (RF)/microwave magnetic devices such as filters, inductors, antennas, and more [1] [2] [3] [4]. These devices are the building blocks for much of today’s technology. FM thin films have been researched for their high magnetic permeability. One major problem with FM thin films is that they tend to have high conductivities. This high conductance leads to eddy currents in the material. It is important to understand magnetic dynamics since it governs the permeability of the material.

2.2 Electromagnetic Properties

In order to understand the measurements in this thesis there is a requirement of understanding certain electromagnetic properties of materials. Electromagnetic materials can be split into two major categories, paramagnetic and diamagnetic.

Diamagnetic materials have completed shells of electrons. Diamagnetism is created by small current loops that are created by orbiting electrons. These orbiting electrons, due to the current loops, create small individual magnetic fields. This field is very small compared to paramagnetism and will be overlooked in this thesis.

Figure 2.1: Electron orbiting Nucleus and Electron spin. [8]
Paramagnetic materials have atoms that shells are not completely filled. Because of the shells not being filled all of the electrons are not paired together with electrons of opposite spin (see figure 2.2). Each electron has a magnetic dipole due to its spin. When all of the dipoles are aligned, because of the unpaired electrons in the outer shell, there is a net magnetism of the material.

Paramagnetism is caused by the spin of the electrons around their own axis. Like the electron orbiting around the nucleus, the spin of the electron creates a magnetic moment. In paramagnetic materials, because of the random position of the atoms due to thermal agitation, in the absence of an external magnetic field, the material does not have a total magnetization. However when an external magnetic field is applied the dipoles of the material are aligned and create a net magnetization.

We will mainly focus on paramagnetic materials from here out. Subcategories of paramagnetic materials are ferromagnetic, anti-ferromagnetic, and ferrimagnetic.
In all paramagnetic materials there is an interaction between neighboring dipoles. This interaction is usually too low to affect the neighboring dipoles. However, below a certain temperature, called the Curie temperature, this interaction is strong enough to affect the neighboring dipoles and create regions of magnetization called domains in the material without having an external magnetic field applied. When this happens the material becomes ferromagnetic. As mentioned before, ferromagnetic materials are usually seen as a hole as non-magnetic. This is due to each domain having its own random orientation. Each of the domain boundaries has some finite thickness where the electron spin changes gradually into the next domain. This area is called the Bloch wall or Neel wall.

The Bloch wall is the area of magnetization whose magnetic vectors rotate perpendicular to the plane of the wall while the Neel wall has magnetic vectors that rotate parallel to the plane of the wall. The Block wall thickness has to due partly with how easily the material is to magnetize in a certain direction. This ease of magnetization is called the easy direction as opposed to the direction of difficult
magnetization, the hard direction. The energy difference that it takes to magnetize the material in the easy direction versus the hard direction is called the magnetic anisotropy energy. The other main contributor to the Block wall thickness is the exchange energy. The exchange energy is the energy between two neighboring moments.

In the application of magnetic materials it is necessary to align all of the domains in a uniform direction. To do this an external magnetic field must be applied to the material. Figure 2.5 shows the magnetization process. The material starts at the origin and as the external magnetic field $\mathbf{H}$ is applied the magnetization of the material $M$ moves to point A (dashed line). Once the external field is removed the magnetization of the material follows the solid line to $M_r$. The pint $M_r$ is known as the remanent magnetization. In order to return the material to zero magnetization a field in the opposite direction must be applied. If an AC field is applied to the material the magnetization follows the solid curve. This is known as the hysteresis loop.

Figure 2.5: Hysteresis loop in a ferromagnetic material. [9]
2.3 Magnetic dynamics
The magnetization of the material can be described by the Landau-Lifshitz-Gilbert (LLG) equation and originated from the model in figure 2.6.

\[
\frac{\partial \mathbf{M}}{\partial t} = -\gamma \mathbf{M} \times \mathbf{H} + \frac{\alpha}{M_0} \mathbf{M} \times \frac{\partial \mathbf{M}}{\partial t}
\]  

(2.1)

where \( \mathbf{H} \) is an effective magnetic field, \( M_0 \) is the magnetic saturation, \( \gamma \) is the gyromagnetic ratio, and \( \alpha \) is the damping constant. The effective magnetic field \( \mathbf{H} \) accounts for the external magnetic field, magnetic anisotropy, and the demagnetization field. This equation can also be seen through the diagram of a spinning electron modeled as a spinning top (figure 2.6).

The LLG equation that is shown here is the non linear model. For most cases this can be changed into the susceptibility tensor.

\[
\chi = \begin{bmatrix}
\chi_{xx} & \chi_{xy} & 0 \\
\chi_{yx} & \chi_{yy} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]  

(2.2)
From this one can obtain the permeability tensor $\hat{\mu}$ where the permeability can be found in the following way

$$\hat{\mu} = \mu_0 \left( I + \chi \right) = -i\mu_a \begin{pmatrix} \mu & i\mu_a & 0 \\ 0 & \mu & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(2.3)

$$\mu = \mu' + j\mu''$$

(2.4)

$$\mu' = 1 + \chi'_{xx} \quad (2.4) \quad \text{and} \quad \mu'' = \chi''_{xx} \quad (2.5)$$

The values $\chi'_{xx}$ and $\chi''_{xx}$ are from separating the real and imaginary parts of the susceptibility tensor.

$$\chi'_{xx} = \frac{\omega M T \omega_0 T \left[ (\omega_0 T)^2 - (\omega T)^2 + 1 \right]}{\left[ (\omega_0 T)^2 - (\omega T)^2 - 1 \right]^2 + 4(\omega_0 T)^2} \quad (2.6)$$

$$\chi''_{xx} = \frac{\omega M T \left[ (\omega_0 T)^2 - (\omega T)^2 + 1 \right]}{\left[ (\omega_0 T)^2 - (\omega T)^2 - 1 \right]^2 + 4(\omega_0 T)^2} \quad (2.7)$$

$$T = \frac{1}{2\pi f_0 \alpha} \quad (2.8)$$

Solving these equations and assuming that the magnetization is saturated and using frequency instead of angular frequency we get

$$\mu' = 1 + 2\pi f A \frac{\gamma M_0}{f^2 - f^2} \quad (2.9)$$
\[ \mu'' = 2\pi \alpha \gamma M_0 f \frac{f_A^2 + f^2}{(f_r^2 - f^2)^2} \]  
\hspace{200pt} (2.10) 

\[ f_A = 2\pi \gamma \left[ H_k + (N_y - N_z)M_0 \right] \]

\[ f_r^2 = 4\pi^2 \gamma^2 \left[ H_k + (N_y - N_z)M_0 \right] \left[ H_k + (N_x - N_z)M_0 \right] \]  
\hspace{200pt} (2.11)

where \( f_A \) is the anti-magnetic resonant frequency, \( f_r \) is the resonant frequency, \( \alpha \) is the Gilbert damping constant, \( H_k \) is the anisotropic magnetic field, \( N_x, N_y, N_z \) are the demagnetization fields.

### 2.4 Magnetic Permeability at RF/microwave Frequencies

Using equations 2.12-2.14 several simulations were performed in MatLab on various materials and are shown in figures 2.7a through 2.7d. The dimension of the material are as follows: length = 2500\( \mu \)m, width = 50\( \mu \)m, and height = 1.5\( \mu \)m.
Figure 2.7b: Complex permeability vs. Frequency

Ms = 2.0, alpha = 0.05, resistivity = 1e-8, hz = 5000

Figure 2.7c: Complex permeability vs. Frequency

Ms = 0.5, alpha = 0.05, resistivity = 1e-3, hz = 5000
In figure 2.7a the FMR is easily seen where the complex (red) part of the permeability reaches a maximum. At this point the real part of the permeability (blue) crosses zero. In these figures, figure 2.7a is used as the baseline while the
saturation magnetization \( (M_s) \), damping coefficient \( (\alpha) \), resistivity \( (\rho) \), and applied dc magnetic field \( (\text{Hz}) \) are changed one at a time in figures 2.7b-e to visualize the effect. In figure 2.7b the resistivity was decreased from \( 1 \times 10^{-3} \text{\Omega m} \) to \( 1 \times 10^{-8} \text{\Omega m} \). In this case the conductivity increased causing eddy currents in the material. The eddy currents block the external magnetic field from penetrating the material thus causing the material to become very lossy. Figure 2.7c shows the plot with \( M_0 \) changed from 2 Tesla to 0.2 Tesla. This decreased and narrowed the FMR dramatically. Figure 2.7d shows the permeability with \( \alpha \) decreased from 0.05 to 0.01 causing the peak of the FMR to increase due to lack of damping. Finally in figure 2.7e the applied DC magnetic field was increased from 5000A/m to 15000A/m causing the peak of the FMR to decrease slightly.

2.5 Scanning Microwave Microscopy Set-up

The equipment used in this experiment was an Agilent 5420 AFM connected to an Agilent Performance Network Analyzer (PNA) N5230C which measures S-parameters (figure 2.8). The AFM 5420 is able to scan both in STM mode and AFM mode. Due to the extreme sensitivity that the AFM has to environmental noise, the location and setup must be chosen with care. In this case the location is in a room isolated from the rest of the building's foundation in order to eliminate vibration. To further isolate the AFM it is placed on a granite block suspended by rubber cords in a box lined with acoustic deadening foam (figure 2.9). Using this setup the AFM 5420 is able to take measurements with true atomic resolution when used in STM mode.
The AFM 5420 has a maximum horizontal scan range of 90µm x 90µm and a maximum vertical scan range of 8µm. This allows a wide range of samples to be tested on this AFM. The minimum resolution, as discussed in chapter 1, is controlled by the width of the tip end.

The AFM 5420 has several different assemblies to perform various measurements. The assembly that we will focus on is used to perform SMM measurements (figure 2.11). The SMM assembly is designed to fit into the same scanner that the normal AFM assembly mounts to.
Figure 2.10: Normal AFM Assembly.

Figure 2.11: Scanning Microwave Microscope Assembly.

Figure 2.12: SMM System.
The SMM assembly has a cable to connect to the PNA. The assembly cable is permanently attached to the SMM assembly in order to make mounting the probe more robust. The cable is connected to a gold contact point that presses against the SMM probe to make a reliable and easy connection to the PNA. Figure 2.13 shows the tip that was used. The probe tip and cantilever is platinum that connects to a gold pad. This is all on a ceramic substrate. The tip radius is less than 20nm [2]. This tip differs from the standard tip only by having a pad that connects the tip to the network analyzer and can be used for traditional AFM measurements.

![Diagram of SMM tip](image)

Figure 2.13: Diagram of SMM tip
The PNA N5230C is a Vector Network analyzer that has a frequency range from 10MHz to 40GHz. The PNA is able to measure the $s_{11}$ parameter which is related to the output signal by the following

$$S_{11} = \frac{V_r}{V_s}$$  \hspace{1cm} (2.12)

where $V_r$ is the reflected signal and $V_s$ is the source or incident signal. The PNA can maintain an extremely accurate measurement of the complex $S_{11}$ parameter due to the fact that not only does it measure the reflected signal but it also measures the incident signal [3].
The SMM system uses the AFM to extract the topography of the sample by reflecting a laser off the end of the cantilever into a photo detector. The change of position of the laser in the photo detector is related to the topography of the sample. The PNA is connected to the AFM probe and as the probe is scanned across the sample collects the $S_{11}$ measurements. In this way the topography and $S_{11}$ measurements are isolated from each other. The connection diagram from the PNA to the SMM probe is shown in figure 2.15.

As seen in figure 2.15 the probe has a 50Ω resistor shunted to it. Because the impedance of most samples is much less than 50Ω, if the resistor was not attached, most of the signal would be reflected back to the PNA due to the mismatch. However the 50Ω resistor brings the impedance of the sample much closer to the network impedance allowing the SMM system and sample to come much closer to matching.
In figure 2.16 the tip was raised into the air and a frequency scan was performed from 2 GHz to 40 GHz while the $S_{11}$ parameter was being measured. Figure 2.16 shows the amplitude (top) and phase (bottom) of the $S_{11}$ parameter. In figure 2.16 one can see distinct envelopes in the amplitude. These envelopes correspond to the resonances of the tip. The multiple peaks are due to the different lengths of waveguides in the system. One other thing worth noting is that as the frequency increases the amplitude drops off significantly above 17 GHz. This is due to the network not matching up for the higher frequencies so most of the signal is reflected in the system before it gets to the tip.

Figure 2.16: Amplitude vs. Frequency and Phase vs. Frequency plot of SMM tip in air from 1.9GHz to 5GHz.
Figure 2.17 shows a narrow frequency scan of one of the peaks. In this figure a more exact measurement of the center of the peak and of the frequency can be obtained. In general the peaks of interest are at the half and quarter wavelength frequencies. These are found by finding a peak that has a phase associated with it of either $0^\circ$ ($\lambda/4$) or $-90^\circ$ ($\lambda/2$).

![Graph of frequency scan](image)

Figure 2.17: Frequency scan of the SMM tip in air from 2.075845GHz to 2.076685GHz

2.6 References


Chapter 3: Experimental Results and Discussions

3.1 Introduction

Development of FM materials over the past three decades that are integrated circuit (IC) compatible magnetic materials with high permeability, high ferromagnetic resonance frequency (FMR), and low losses has been a significant challenge [5] [6]. Recently thin film ferrite materials have been looked at for integrated circuits due to their low conductivity and high resonance frequency. Integrating these materials into standard complementary metal-oxide-semiconductor (CMOS) technology has been difficult due to the following issues. First is the high processing temperatures for ferrite film that comes through the deposition or growth method. Several ways exist to deposit ferrite films, liquid phase epitaxy (LPE) (>950°C), Pulsed Laser Deposition (PLD) (>850°C), and Sputtering (800°C). Out of all the methods mentioned only one has a lower processing temperature than the post processing temperature of standard CMOS technology (475°C) which is sputtering. The next difficulty is Snoek's frequency limit. Snoek's limit is the product of static permeability $\mu_s$ and the resonance frequency $f_r$,

$$\mu_s - 1 = \frac{2(4\pi M_s)}{3H_k}$$  \hspace{1cm} (3.1)
\[ f_r = \frac{\gamma H_k}{2\pi} \]  

Combining equations 2.1 and 2.2 give Snoek's limit to be

\[ L_s = (\mu_s - 1)f_r = \frac{\gamma}{2\pi} 4\pi M_s \]

where \( \gamma \) is the gyromagnetic ratio, \( M_s \) is the saturation magnetization, and \( H_k \) anisotropic magnetic field [7]. Based on this relationship there is a significant trade off. As \( f_r \) increases, \( \mu_s \) decreases. Another difficulty is the need for external biasing magnetic fields.

Recently however, low-temperature spin-sprayed ferrite films (Fe$_3$O$_4$) with a high self-biasing magnetic anisotropy field have been reported. This material shows a FMR frequency greater than 5 GHz. These types of film hold great potential for RF/microwave devices and have immediate applications in patch antennas and bandpass filters. The temperature-dependent electrical resistivity of Fe$_3$O$_4$ has been reported by a few groups to have a higher resistivity at the grain boundary than the grains of the Fe$_3$O$_4$. This was determined by performing resistivity measurements over a large area that crossed multiple grain boundaries. The model shows that the grain boundaries form potential barriers that prevent tunneling current between the grains. At this time there are few publications that deal with in situ characterization of electrical resistivity of a single grain boundary and the measurements were made at zero or low frequencies. In 2012 [16] [17] in situ SMM characterization of a thin Fe$_3$O$_4$/Photoresist/Fe$_3$O$_4$ film at frequencies between 2.0
GHz and 8.0 GHz were performed by our group. This method concurs with the previous method to show that the grain boundaries have higher electrical conductivity than the grains.

3.2 Experiments

In this experiment we used a sample with spin sprayed Fe$_3$O$_4$(1.2 µm)/Photoresist (30 nm)/Fe$_3$O$_4$(1.2 µm) on a glass substrate. The Fe$_3$O$_4$/Photoresist/Fe$_3$O$_4$ multilayer was created by spin spray at 90º C onto a 0.1 mm glass substrate. An oxidation solution with 2 mM NaNO$_2$ and 140 nM CH$_3$COONa with a pH value of 9 and a precursor solution of 10 mM Fe$^{2+}$ and a pH of 4 were sprayed simultaneously through two nozzles onto a glass substrate rotating at 145 rpm in N$_2$ gas. The growth rate was ~40nm/min. When the layer thickness was approximately 1.2µm a layer of photoresist was added by spin spray at 2500 rpm for 30 sec. This was then annealed at 100ºC for 10 min to form a 60 nm non-magnetic layer. After this another layer of Fe$_3$O$_4$ was deposited onto the photoresist layer to complete the sample. The photoresist layer served as an insulation layer to prevent current flow between the two ferrite layers. The film exhibited in-plane coercivity of 118 Oe, saturation magnetization of 398 emu/cm$^3$, and electrical resistivity of 7 Ω cm. The magnetic properties of the material was measured using a vibrating sample magnetometer with an external magnetic field applied in parallel (in plane) and perpendicular (out of plate) to the film plane. The ferromagnetic resonance spectrum was obtained using an electron paramagnetic resonance system operating at X-band (9.6 GHz) with an external magnetic field applied parallel to the film plane and was shown to be 464 Oe. The complex permeability spectra was measured by a broad band,
custom made permeameter consisting of a coplanar waveguide connected to a network analyzer with a bandwidth of 0.045 to 10 GHz. The film demonstrated a FMR frequency of 1.2 GHz. In situ electrical characterization was performed on an Agilent 5420, which consists of an AFM and a microwave network analyzer. The PNA records one-port scattering parameters ($S_{11}$) in a broad frequency range from 2.0 GHz to 40 GHz. During the SMM measurement, $S_{11}$ was measured and read out by the PNA on a different channel from the surface morphology measured by AFM. This assures decoupling between the surface morphology and the microwave images. Based on the transmission line theory, the amplitude and phase of the scattering parameter reflect the electromagnetic properties of the samples. The spatial resolution of SMM can be approximately estimated as equal to the tip radius ($\sim30$ nm) due to the enhanced electromagnetic field at the tip end.

### 3.3 Results and Discussions

Figure 3.11 shows the measured complex magnetic permeability of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ sample. Simulations were also performed based on the parameters listed in table 1. The Landau-Lifshitz phenomenological damping constant $\alpha$ was assumed to be about 0.46 in the simulation to obtain a reasonable fit even though the measured value was around 0.011. The difference can be partly explained by the lack of an external magnetic field where the measurement was performed in a strong external magnetic field. The VSM measurements showed that there was no preferred in-plane magnetization direction.
Figure 3.1: Simulated and Measured complex permeability spectra.

<table>
<thead>
<tr>
<th>Film Structure</th>
<th>Thickness (µm)</th>
<th>M_s (emu/cm³)</th>
<th>H_k (Oe)</th>
<th>μ'</th>
<th>ΔH (Oe)</th>
<th>ρ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>2.4</td>
<td>183.0</td>
<td>200.0</td>
<td>10.0</td>
<td>464.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The surface morphology of the Fe₃O₄/Photoresist/Fe₃O₄ showed pebble-stone shaped particles with sizes ranging from a few hundred nanometers to a few
microns. The magnitude of the complex reflection coefficient was recorded by SMM shown in Figure 3.2b and e.

Prior to each SMM imaging, a frequency scan over the range of 0.5-6.0 GHz was performed, and typically a number of resonant peaks could be registered. To improve the accuracy and sensitivity, the SMM image was recorded in contact mode and in the vicinity of the sharpest resonance peaks ($f=2.3909$ GHz). Compared to Figure 3.2b, there is a clear contrast between the inner grains and the boundaries in Figure 3.2e. The amplitude of the reflection coefficient from the grain boundaries is higher than those from the inner grain region, as manifested by bright lines for the grain boundaries and black holes for the grains. The surface morphology and the reflection coefficient were measured and read out through different channels (i.e., laser diode for surface morphology, PNA for SMM), ensuring decoupling between the surface morphology and the SMM image. The contrast in Figure 3.2b thus reflects solely the response of RF/microwave signals due to the different electrical properties of the materials. Systematic measurements were taken of the Fe$_3$O$_4$/Photoresist/Fe$_3$O$_4$ multilayer at each peak of the frequency scan. Before the SMM measurements three scans were taken of the SMM tip in air. These scans ranged from 2.0 to 2.6 GHz, 4.06 to 5.27 GHz, and 5.86 to 7.93 GHz. After the frequency scan of the SMM tip, three SMM images were recorded for each of the numbered peaks (See Appendix A). Images to the left are the topography of the sample. The topography was measured in contact mode. Each of the measurements was taken from the same location on the multilayer sample. The center image shows the measured $S_{11}$ parameter and the right images show the measured phase.
<table>
<thead>
<tr>
<th>Figure 3.2a: Topography of multilayer at λ/2.</th>
<th>Figure 3.2d: Topography of multilayer at λ/4.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Topography of Multilayer at λ/2" /></td>
<td><img src="image2.png" alt="Topography of Multilayer at λ/4" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Figure 3.2b: Amplitude of multilayer at λ/2.</th>
<th>Figure 3.2e: Amplitude of multilayer at λ/4.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image3.png" alt="Amplitude of Multilayer at λ/2" /></td>
<td><img src="image4.png" alt="Amplitude of Multilayer at λ/4" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Figure 3.2c: Phase of multilayer at λ/2.</th>
<th>Figure 3.2f: Phase of multilayer at λ/4</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Phase of Multilayer at λ/2" /></td>
<td><img src="image6.png" alt="Phase of Multilayer at λ/4" /></td>
</tr>
</tbody>
</table>
Two of the samples are particularly interesting because they fall at the half-wavelength and quarter-wavelength frequencies. Figures 3.2a-c shows the λ/2 case with the frequency set at 2.486832 GHz and a phase of -93.387917°. Figures 3.2 d-f shows the λ/4 case with the frequency set at 6.268777 GHz and a phase of -2.810643°. Comparing the half-wavelength amplitude and the quarter-wavelength amplitude the contrast of the grain boundary and the grain is reversed: the grain boundary was bright in contrast to the grains in the half-wavelength case, while it becomes dark relative to the grains in the quarter-wavelength case. This frequency-dependent contrast verifies the decoupling of the SMM images from the surface topography. It is worth mentioning that s_{11} depends on both the dielectric and magnetic properties of the sample. From the magnetic permeability spectra measurement, above the ferromagnetic resonant frequency ~ 1.2 GHz, the magnetic permeability decreased significantly. At operating frequency above 2.0 GHz the magnetic permeability drops to less than 1.5. Hence, the contribution of the magnetic permeability in the SMM measurements becomes negligible. The complex dielectric constant ε in general depends on the operating frequency (ω, angular frequency), the real part of the dielectric constant (ε'), and the conductivity of the sample (σ):

\[
\varepsilon = \varepsilon' + \frac{\sigma}{j\omega}
\]

(3.4)
Therefore, changes of either $\varepsilon'$ or $\sigma$ will lead to variations of the reflected signal $S_{11}$.

To further investigate the correlation between the SMM images and electric properties of the sample, a model of the SMM circuit was created (figure 3.3). The model consists of a transmission line with length $l$ and characteristic impedance $Z_0 = 50 \Omega$. The length of the transmission line was designed to be approximately equal half wavelength ($\lambda$) at 2.5 GHz. The load of the transmission line contains a shunt resistive component to represent the conductivity of the sample and a shunt capacitive component to represent the dielectric property. Since the physical ground in the SMM system is 3 mm away from the SMM tip, the load can be, in general, considered as an open circuit (i.e. $R \gg Z_0$, and $\frac{1}{C} \gg Z_0$) with perturbed resistance and capacitance contributed by the sample. Such perturbation is significantly enhanced by using a nanoscale tip. To improve the sensitivity the whole transmission line is shunted with a 50$\Omega$ resistor. As for a one-port system, according to transmission line theory, $S_{11}$ is equal to the reflection coefficient $\Gamma$ and can be written as

\[ S_{11} = \Gamma \]
\[
\Gamma = -\frac{Z_0 + jZ_L \tan(\beta l_0)}{(Z_0 + 2Z_L) + j(2Z_0 + Z_L) \tan(\beta l_0)}
\] (3.5)

where

\[
Z_L = \frac{1}{\frac{1}{R} + j\omega C}
\] (3.6)

In these equations \(\Gamma\) is the reflection coefficient, \(Z_0\) is the parasitic impedance (50Ω), \(Z_L\) is the impedance of the sample where \(R\) and \(C\) are the resistance and capacitance of the sample due to the complex nature of \(Z_L\), \(\beta\) is the wave number, and \(\omega\) is the angular frequency. To further investigate this model the equation was further simplified so that the relation between \(\omega, C,\) and \(R\) could be extracted. If the frequency approaches half-wavelength the following equation simplifies to

\[
|\Gamma| \approx \frac{Z_0}{2} \sqrt{\frac{1}{R^2} + \omega^2 C^2}
\] (3.7)

and

\[
\theta \approx \tan^{-1}(\omega RC)
\] (3.8)

In practice, the \(\lambda/2\) resonance was recognized by choosing the peak with phase angle \(\theta \approx -\left(\frac{\pi}{2}\right)\) because when the SMM tip was lifted up in the air, \(R\) approached infinity leading to phase angle close to \(\theta \approx -\left(\frac{\pi}{2}\right)\). At onset of \(\lambda/2\) resonance, high
electrical conductivity, i.e., low resistivity, will lead to a larger value of $|\Gamma|$ but a smaller value of $\theta$ while high dielectric constant will increase $|\Gamma|$ and $\theta$ simultaneously. This principal can be seen in the SMM images taken in figures 3.12a-c. The above argument is supported by performing SMM measurements at $\lambda/4$ resonance. When the frequency approaches the $\lambda/4$ resonant frequency, the amplitude $|\Gamma|$ and the phase angle $\theta$ can be simplified from equation 1 to be

$$|\Gamma| \approx 1 - 2Z_0 \sqrt{\frac{1}{R^2} + \omega^2 C^2}$$  \hspace{1cm} (3.9)$$

and

$$\theta \approx -\tan^{-1}(2Z_0 \sqrt{\frac{1}{R^2} + \omega^2 C^2})$$  \hspace{1cm} (3.10)$$

At onset of $\lambda/4$ resonance, materials with high electrical conductivity will have smaller values of $|\Gamma|$ and $\theta$. In practice, the $\lambda/4$ resonance was recognized by choosing the peak with phase angle $\theta \approx 0$. The SMM images shown in figures 3.13d-f show this principal. To further demonstrate this principle a MatLab simulation was conducted of equation 3.5 and plots were developed of $|\Gamma|$ vs. $R$ and $\theta$ vs. $R$ for both the half-wavelength and quarter-wavelength cases. The resulting plots are shown in figure 3.4.
These results match with the measurements taken at the half and quarter wavelength frequencies. In the SMM measurement images for the $\lambda/2$ case one can see from figure 3.2b that the grains have lower amplitude than the grain boundaries. Comparing this to the MatLab simulation the results in the grains have a lower conductivity (higher resistivity) than the grain boundaries. For the quarter-wavelength case the SMM measurement images show that the grains have a higher reflection coefficient than the grain boundaries which also means that the grains have a higher conductivity than the grain boundaries. In this case the plots agree with the relationships developed through the simplified equations.
Measurements of a reference sample (graphene oxide/platinum) with known conductivity/resistivity and the ferrite multilayer were performed at the same frequency to further validate the above discussions and are compared in figure 3.5a-d.

Figure 3.5a: Surface morphology of multilayer.
Figure 3.5b: Amplitude of the reflection coefficient.
Figure 3.5c: Surface morphology of the graphene oxide/Pt sample.
Figure 3.5d: Amplitude of the reflection coefficient of the graphene oxide/Pt sample at 3.3909 GHz.

The reference sample contains a 5-nm-thick, partially oxidized graphene nanosheet on a conductive platinum surface. It is well known that oxidized graphene is not a
good conductive material. In figure 3.5d, the platinum substrate appears to be bright in contrast, while the area coated with graphene oxide nanosheets appears dark in contrast, indicating an amplitude enhancement of $S_{11}$ by electrical conductivity at this frequency. Comparing this with figure 3.5b suggests that grain boundaries are more conductive than the grains of the ferrite multilayer. This observation is consistent with the findings of Visoly-Fisher et al. [5], who discovered a conductive path for electrons along the grain boundary, which proves to be beneficial for the performance of poly-crystalline solar cells. According to the grain boundary space-charge regions [6] [7] [8], accumulation of charges in the space-charge region has been revealed by a number of groups [9] [10] [11]. The accumulated charges, we believe, play an important role in the enhancement of the local grain-boundary. Perpendicular to the grain boundary, the two adjacent space-charge regions can be considered as double Schottky barriers [6], blocking current flow from grain to grain, and imposing high resistance across the grain boundary.

3.4 References


Chapter 4: Conclusion

4.1 Various Experimental Results

This chapter introduces the experimental results that were obtained for testing highly oriented pyrolytic graphite (HOPG). HOPG is a stack of two dimensional graphene sheets. Graphene is tightly packed carbon atoms into a hexagon lattice [1]. Graphene has been heavily studied for the past few years because of its unique properties such as a high thermal conductivity, high electron mobility, transparency, and strength. In this experiment we are able to measure the local conductivity of HOPG using the SMM.

Experiment

The HOPG was prepared by using tape to peel off the top layer of graphite. This allowed the formations of ribbons on the surface of the HOPG. The HOPG was then measured using an SMM. The SMM tip was raised slightly above the surface of the HOPG and a frequency scan was performed to get the open reflection coefficient from 2 GHz to 8 GHz. As stated in the previous chapter, a careful examination of the peaks in the amplitude were compared with the phase and two frequencies were pick out to be the quarter wavelength and half wavelength frequencies of the system (6.269014 GHz and 4.750884 GHz respectively). The tip of the SMM was then
lowered onto the HOPG in constant contact mode and raster scanned across the surface at each frequency.

**Measurements**

Figure 4.1 shows HOPG measured by an AFM/SMM. These measurements were taken at a frequency of 6.269014GHz with a phase of -3.9 degrees. This would indicate that this is the quarter wavelength frequency. One can distinctly see the ribbons of graphene with a mostly vertical orientating. Figures 4.1 b and 4.1c show the amplitude and phase of the $s_{11}$ measurement respectively. In these figures we can clearly see a change of amplitude and phase on the edge of each ribbon denoting a change in local conductivity. To help see this difference a cross sectional view has been provided in Figure 4.2.

![Figure 4.1a: HOPG at λ/4 topography](image)
Figure 4.1b: HOPG at $\lambda/4$ $s_{11}$ amplitude.

Figure 4.1c: HOPG at $\lambda/4$ $s_{11}$ phase.
Figures 4.2a-c show the HOPG measurements at the half wavelength frequency at 4.750884GHz and a phase of -96.9 degrees.
Figure 4.3a: HOPG at $\lambda/2$ topography

Figure 4.3b: HOPG at $\lambda/2$ amplitude
Figure 4.3c: HOPG at $\lambda/2$ phase.

Figure 4.4a: HOPG topography cross section view

Figure 4.4b: HOPG $s_{11}$ amplitude cross section view
4.2 Future Works

The future of nanomaterials depends heavily on the ability to characterize their properties. In recent years great strides have been made toward this goal. SMM is one of the bright spots in this research. For SMM to remain an asset in characterizing nanomaterial there are a few advances that must be accomplished. At present SMM can only be used for qualitative measurements. A value for local conductivity cannot be found using SMM. In this section a possibility for the calibration of the SMM will be introduced. This will allow the SMM to be used to obtain quantitative measurements as well. This calibration will be based on the calibration for one-port systems at RF and microwave frequencies. The
calibration requires three measurements on known standards (A, B, and C) to extract the three systematic errors \((E_d, E_r, \text{ and } E_s)\) shown in figure 4.5. These three systematic errors are found by solving

\[
S_{11-j}^m = E_d + \frac{S_{11-j}E_r}{1 - S_{11-j}E_s} \quad (j = A, B, C)
\]  

(4.1)

where \(S_{11-j}^m\) and \(S_{11-j}\) are the measured \(S_{11}\) parameters on the known loads (A, B, and C) with and without systematic errors respectively. The calibration standards proposed for this are a conducting plate, impedance-matching plate, and air. The novel calibration substrate (CASUB) that is proposed is shown in figure 4.6.

On the CASUB the electrical ground is designed to contact the ground of the SMM probe. In order to connect the substrate to the SMM ground, the SMM system will
have to be modified with a conducting chuck to have the electrical ground of the SMM directly connected to the sample holder. This will allow the transmission line to be formed by the tip (signal line) and the conducting chuck (electrical ground). The CASUB is proposed to be fabricated on a 3-inch silicon substrate covered with thin metallic films on both sides. A floating ground is formed by connecting the two metallic layers through the vias (see figure 4.6). The calibration on the conducting plate will be performed by setting the SMM tip on the top of the floating ground with the backside connected to the chuck. Also an array of varying sized capacitors will be formed on the CASUB [2]. The known capacitance, determined by the pattern size and the thickness of the CASUB, will be used for calibration of matching impedance. The air calibration will be performed by lifting the SMM tip above the CASUB. The reflection coefficients of the three proposed calibration standards are given by

\[
S_{11-\text{conducting-plate}} = -1 \\
S_{11-\text{impedance-matching}} = \frac{1}{j\omega C} - Z_0 \\
S_{11-\text{air}} = 1
\]

where \( \omega \) is the angular frequency, \( C \) is the capacitance, and \( Z_0 \) is the characteristic impedance of the system. After the calibration, the reference plane for RF/microwave characterization will be shifted to the end of the SMM tip.
4.3 References


Publications


Appendix A

Appendix C contains systematic measurements taken of the Fe$_3$O$_4$/Photoresist/Fe$_3$O$_4$ multilayer. These measurements were used to discover the quarter wavelength and half wavelength frequencies and show how the $s_{11}$ amplitude and phase change according to different frequencies.
Peak 2

Frequency: 2.079865 GHz  Phase: 179.832184  Left of Peak

Frequency: 2.080751 GHz  Phase: 124.606598  Center of Peak

Frequency: 2.081622 GHz  Phase: 70.911423  Right of Peak

Peak 6
Frequency: 2.266737 GHz  Phase: 178.536072  Left of Peak

Frequency: 2.269019 GHz  Phase: -153.980118  Center of Peak

Frequency: 2.271301 GHz  Phase: -126.993393  Right of Peak

Peak 8
Frequency: 2.389772 GHz  Phase: 98.670311  Left of Peak

Frequency: 2.390507 GHz  Phase: 149.842636  Center of Peak

Frequency: 2.391258 GHz  Phase: -158.382462  Right of Peak

Peak 9
Frequency: 2.439045 GHz  Phase: -22.34351  Left of Peak

Frequency: 2.440072 GHz  Phase: -67.231827  Center of Peak

Frequency: 2.441099 GHz  Phase: -11.517624  Right of Peak

1.5
Peak 10

Frequency: 2.485826 GHz  Phase: -37.419456  Left of Peak

Frequency: 2.486832 GHz  Phase: -93.387917  Center of Peak

Frequency: 2.487838 GHz  Phase: -148.074905  Right of Peak
Peak 1

Frequency: 4311137 GHz  Phase: -77.453522  Left of Peak

Frequency: 4.112922 GHz  Phase: -125.580231  Center of Peak

Frequency: 4.11508 GHz  Phase: 179.923813  Right of Peak
Peak 2

Frequency: 47.193224 GHz  Phase: -16.14157  Left of Peak

Frequency: 4.195361 GHz  Phase: 50.500015  Center of Peak

Frequency: 4.197497 GHz  Phase: 55.67794  Right of Peak
Peak 3

Frequency: 4.346298 GHz  Phase: 179.974442  Left of Peak

Frequency: 4.348425 GHz  Phase: 112.715446  Center of Peak

Frequency: 4.350517 GHz  Phase: 47.060234  Right of Peak
Peak 4

Frequency: 4.405964 GHz  Phase: -123.864456  Left of Peak

Frequency: 4.407975 GHz  Phase: -99.987434  Center of Peak

Frequency: 4.409986 GHz  Phase: -76.995132  Right of Peak
Peak 5

Frequency: 4.464693 GHz  Phase: 179.878876  Left of Peak

Frequency: 4.466208 GHz  Phase: -120.447479  Center of Peak

Frequency: 4.467737 GHz  Phase: -61.747265  Right of Peak
Peak 6

Frequency: 4.520369 GHz  Phase: 163.529099  Left of Peak

Frequency: 4.521482 GHz  Phase: -152.434174  Center of Peak

Frequency: 4.522595 GHz  Phase: -109.092102  Right of Peak
Peak 7

Frequency: 4.63877 GHz  Phase: 27.412617  Left of Peak

Frequency: 4.639961 GHz  Phase: -40.046394  Center of Peak

Frequency: 4.641152 GHz  Phase: -103.023735  Right of Peak
Peak 8

Frequency: 4.856486 GHz  Phase: -92.877441  Left of Peak

Frequency: 4.85726 GHz  Phase: -162.42453  Center of Peak

Frequency: 4.858031 GHz  Phase: 134.273865  Right of Peak
Peak 9

Frequency: 4.920441 GHz  Phase: -103.166557  Left of Peak

Frequency: 4.921229 GHz  Phase: 169.654373  Center of Peak

Frequency: 4.922053 GHz  Phase: 99.890526  Right of Peak
Peak 10

Frequency: 5.176269 GHz  Phase: 102.604111  Left of Peak

Frequency: 5.177991 GHz  Phase: 46.644257  Center of Peak

Frequency: 5.179773 GHz  Phase: -10.125202  Right of Peak
Peak 11

Frequency: 5.216327 GHz  Phase: 88.990242  Left of Peak

Frequency: 5.218502 GHz  Phase: 40.547955  Center of Peak

Frequency: 5.220677 GHz  Phase: -9.0808  Right of Peak
Peak 1

Frequency: 6.174624 GHz  Phase: 103.995453  Left of Peak

Frequency: 6.176926 GHz  Phase: 42.291103  Center of Peak

Frequency: 6.179203 GHz  Phase: -18.75963  Right of Peak
Peak 2

Frequency: 6.21995 GHz  Phase: 95.191818  Left of Peak

Frequency: 6.221145 GHz  Phase: 20.326504  Center of Peak

Frequency: 6.22234 GHz  Phase: -44.22818  Right of Peak
Peak 3

Frequency: 6.267727 GHz  Phase: 62.864513  Left of Peak

Frequency: 6.268777 GHz  Phase: -2.810643  Center of Peak

Frequency: 6.269862 GHz  Phase: -70.044563  Right of Peak
Peak 4

Frequency: 6.314413 GHz  Phase: 30.13586  Left of Peak

Frequency: 6.316618 GHz  Phase: -27.984579  Center of Peak

Frequency: 6.318823 GHz  Phase: -86.020889  Right of Peak
Peak 5

Frequency: 6.360979 GHz  Phase: 13.492931  Left of Peak

Frequency: 6.363074 GHz  Phase: -41.122894  Center of Peak

Frequency: 6.365214 GHz  Phase: -95.754028  Right of Peak
Peak 6

Frequency: 6.408159 GHz  Phase: 73.169052  Left of Peak

Frequency: 6.409791 GHz  Phase: 124.395256  Center of Peak

Frequency: 6.411424 GHz  Phase: 171.302414  Right of Peak
Peak 7

Frequency: 7.331764 GHz  Phase: -84.395058  Left of Peak

Frequency: 7.332408 GHz  Phase: -154.623108  Center of Peak

Frequency: 7.333027 GHz  Phase: 143.925232  Right of Peak
Peak 8

Frequency: 7.4752 GHz  Phase: 179.703018  Left of Peak

Frequency: 7.476453 GHz  Phase: 126.117302  Center of Peak

Frequency: 7.477761 GHz  Phase: 72.664032  Right of Peak
Peak 9

Frequency: 7.519767 GHz  Phase: 179.77786  Left of Peak

Frequency: 7.522819 GHz  Phase: 105.38382  Center of Peak

Frequency: 7.525828 GHz  Phase: 26.874325  Right of Peak
Appendix B

Appendix D shows step by step instructions on how to take measurements using the SMM.

1) Place the scanner in the mounting fixture.

2) Place the nose assembly onto the scanner. Make sure that the notch on the nose assembly matches up with the pin inside of the scanner. Press firmly and evenly down on the nose assembly until the nose assembly is completely seated (see figure).

3) Use the SMM tool to lift the contact point.

4) Pick the SMM tip up using tweezers and slide the tip into place. Make sure that the gold plate on the tip is touching the contact point on the nose assembly. This part is extremely difficult and should be practiced using a broken tip until mastered.

5) Release the extraction slides so that the tip can move freely.

6) Mound the scanner into the AFM.
7) Conned the Scan HV and Scan LV to the AFM and the cable to the PNA.

8) Turn on the controller and laser.

9) Open the PicoView 1.6.4 software on the computer.

10) If the camera view is not on you can activate it by going to Controls... Camera View.

11) Align the laser so that it is on the very tip of the cantilever and so that you get a strong reflection where the photo detector will go.
12) Close the Camera View.

13) Insert the photo detector and connect it to the AFM.

14) Align the dot so that it is in the center of the Laser Alignment window and so that the voltage is above 6.

15) Turn on the PNA.

16) Turn on the voltage generator. Make sure that V1 is set to 5 volts and V2 to 7 volts.

17) On the PNA go to the desktop and click on the PnaSvr Icon.

18) Click on Run Regression Test.

19) When it asks if you are sure you want to run the test click yes.
20) Bring the tip close to the sample using the Open and Close switch on the controller.

21) In the PicoView window click on Controls...Setup...Options

![Agilent Technologies PicoView 1.6](image)

22) Place a check mark in the box labeled Agilent PNA and then close the Options box.
23) Click on Controls . . . PNA to bring up the PNA controller.

24) Bring the tip down to meet the sample by pressing the Approach button.

25) Once the tip is down you may start scanning the sample.
26) Set the desired Sweep Start and Sweep End frequencies.

27) Click on the Sweep button.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Level (dBm)</td>
<td>5.00</td>
</tr>
<tr>
<td>Scan Frequency (GHz)</td>
<td>2.000000</td>
</tr>
<tr>
<td>Sweep Start (GHz)</td>
<td>2.000000</td>
</tr>
<tr>
<td>Sweep End (GHz)</td>
<td>5.000000</td>
</tr>
<tr>
<td>Sweep Points</td>
<td>1000</td>
</tr>
<tr>
<td>Capacitance Coefficient (FF/db)</td>
<td>1.000</td>
</tr>
<tr>
<td>Phase Offset (°)</td>
<td>0</td>
</tr>
<tr>
<td>IFBW (Hz)</td>
<td>1000</td>
</tr>
<tr>
<td>Trigger</td>
<td>BNC</td>
</tr>
<tr>
<td>PNA Computer Name</td>
<td>192.168.2.100:45454</td>
</tr>
</tbody>
</table>