Nano-Materials for Microwave and Terahertz Applications

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NANO-MATERIALS FOR MICROWAVE AND TERAHERTZ APPLICATIONS

A dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

By

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Abstract


In this age of digital electronics the quest for faster computational devices and high speed communications have driven a need for new materials that are capable of fulfilling these goals. In both areas the need for a thinner channel in transistors, faster carrier transport characteristics, and better magnetic materials dominate the direction of research. Recently 2D materials have been realized. These single layer atomic thick materials show potential in having extremely high carrier transport velocities at room temperature and, due to their natural 2D structure, are the thinnest material possible in nature. On the other hand spin-spray ferrites have showed potential in producing high permeability, low loss materials with a low processing temperature compatible with current CMOS technology. One of the largest hindrances in the implementation of these materials are the lack of measurement capabilities. Both 2D materials and spin-spray ferrites have nm sized features that significantly change how the material behave. To further investigate these materials scanning microwave microscopy (SMM) is being developed as a possible characterization tool. SMM has the unique ability to collect the complex reflection coefficient simultaneously with the topography at nm horizontal spatial resolutions. The complex reflection coefficient is able to supply valuable information about materials such as conductivity and permittivity. This dissertation provides an in depth look at the potential applications for SMM and supplies a rigorous characterization, both
experimentally and numerical simulations, of the SMM system. In detail we report first time SMM measurements of graphene’s conductivity and permittivity along with characterization of graphene defects induced by oxygen plasma etching and graphene wrinkles. We have also experimentally show conductive grain boundaries in spin-spray ferrites leading to larger than expected losses. Lastly we show Fourier transform inferred spectroscopy measurements of graphene micro and nano ribbons. These results show the versatility of SMM and the ability to further characterize new materials. Furthermore we show the ability of the SMM to obtain calibrated conductivity and permittivity measurements on the nanoscale level leading to a more complete understanding of the effects of defects on the electrical properties of graphene and understanding of the losses in ferrimagnetic materials.
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1 Introduction

1.1 2-D Materials

2D Materials have been theorized since the early 1900’s [1]. However few people believed that they could exist in nature due to their being thermodynamically unstable [2]. In 2004 however Andry Geim and Konstantin Novoselov experimentally demonstrated that 2D materials could indeed exist in nature [3]. In their founding paper “Electric Field Effect in Atomically Thin Carbon Films”, a method of exfoliating highly oriented pyrolytic graphite (HOPG) was demonstrated and achieved few layer down to mono-layer graphite films. These films showed extremely large electron mobilities ($\mu_e > 200,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) [4], great thermal conductivity ($\kappa = 1250\text{Wm}^{-1}\text{K}^{-1}$) [5], and record intrinsic strength ($\sigma_{int} = 130\text{GPa}$) [6] compared to that of steel ($\sigma_{int} = 550\text{MPa}$). All of these exotic properties propelled research into other 2D materials. 2D materials can be broken down into three main groups, layered van der Waals solids, layered ionic solids, and surface assisted nonlayered solids [7]. Of the layered van der Waals solids graphene has been the most studied. Other materials include hexagonal boron nitride, and transition metal dichalcogenides (TMD) such as MoS$_2$ (fig. 1), MoSe$_2$, and WS$_2$. These materials, as their name suggests, have single atomic thick layers that have strong in-plane bonding but are weakly held together out of plane by van der Waals forces with a bonding typically in the range of 40-70 meV. Furthermore the TMDs show great promise in that, unlike graphene, some have a band gap brought about by a buckled state. Currently there are over 40
Figure 1: MoS$_2$ Atomic Structure representing a layered van der Walls solid [8, 9].

Figure 2: Crystal structure of KCa$_2$Nb$_3$O$_{10}$ representing a layered ionic solid (left). Atomic structure of Silicene representing a surface assisted nonlayered solid (right) [12, 7].

know TMDs. Although TMDs have a band gap the mobility is very low compared to that of graphene (~900 cm$^2$/V\text{s}) [10] making them a poor choice for high speed electronics.

Layered ionic solids take the form of bulk crystals with charged 2D polyhedral layers [11]. These layers are predominately held together by strong electropositive cations or strongly electronegative anions and are sandwiched between hydroxide or halide. Perovskite type oxides La$_{0.90}$Eu$_{0.05}$Nb$_2$O$_{10}$ and KCa$_2$Nb$_3$O$_{10}$ (Fig. 2), metal hydroxides Eu(OH)$_{2.5}$\textit{DS}$_{0.5}$, Ni(OH)$_{2-x}$, and cation-exchanged layered metal oxides LiCoO$_2$, Na$_2$Ti$_3$O$_7$ are all examples of layered ionic solids. These materials have applications in high-\textit{x} dielectrics and wide band gap semiconductors.

The third group of 2D materials are surface assisted nonlayered solids. These materials are typically deposited onto substrates by chemical vapor deposition (CVD)
and epitaxial growth. A few of these materials are Silicene/Ag(111) (fig. 2), Al₂O₃/SiO₂, and TiO₂(material/substrate). These materials are typically used as insulators but silicene however has been identified as a possible replacement for bulk silicon in transistor applications. The largest issue currently with silicene is its instability in the atmosphere due to its high rate of oxidation. Because of this silicene has only been formed in vacuums.

Due to the various uses of graphene and the previous research that has already been performed this dissertation will focus on graphene.

1.2 Graphene

Graphene is the two dimensional alatrop e of graphite. It was found in 2004 by Andry Geim and Konstantin Novoselov. By pealing apart layers of highly ordered pyrolytic graphite (HOPG) using tape they were able to form single layer graphite (graphene) [3]. This was the final discovery of the single layer carbon structure starting with the 0D buckyball, 1D carbon nanotube, and finally the 2D single layer of graphite (graphene) (Fig. 3). This material has been shown to have remarkable properties already discussed in section 1.2. Graphene is a tightly packed 2D honeycomb structure of carbon atoms (Fig. 3). Graphene acquires its honeycomb structure from the sp² hybridization bonding (Fig. 4). The carbon atoms are connected together by strong coupling between the three sp² orbitals leading to the σ-bonds, while the pₓ orbitals lead to π-bonds. These π-bonds lead to the delocalized π-electrons and
Figure 4: Diagram of graphene electron orbitals showing the sp² orbitals in the plane along with the pₓ orbitals. The pₓ orbitals combine to form a continuous electron cloud over the top and bottom of the graphene sheet. [15]

Figure 5: Band structure of a normal (parabolic) semiconductor band structure (left) and graphene’s linear band structure. [16]

give rise to the ballistic transport of the electrons through the graphene sheet at room temperature and allows graphene to exhibit 2D electron gas (2DEG) structure. One of the most interesting properties of graphene is its band structure. Unlike traditional semiconductors where the band structure is parabolic, graphene exhibits a linear structure. The linearity comes from the massless dirac fermions (MDF) of the graphene and are described as follows.

\[ E = \hbar v_F |k| \]  

\[ E = \frac{\hbar k^2}{2m^*} \]  

Eq. 1 represents the relativistic Dirac band structure of graphene and Eq. 2 represents the non-relativistic Schrodinger band structure of a traditional semiconductor.
material. In this case $E$ is the energy, $\hbar$ is the reduced Planck constant, $v_F$ is the fermi velocity, $k$ is the momentum, and $m^*$ is the effective mass. A diagram of this can be seen in Fig. 5. These equations demonstrate that, unlike traditional semiconductor materials, $v_F$ of graphene does not depend on the effective mass of its carriers [17]. These MDFs give rise to the extremely high mobilities that are found in graphene.

One of the major drawbacks to graphene is the lack of a band gap [18]. Many attempts of opening a bandgap in graphene have been attempted with little success [19, 20, 21] including nano-ribbons, doping, multilayer graphene, and substrate induced bandgap opening. The largest problem with the opening of a bandgap is the introduction of defects and impurities into the graphene. Using nano-ribbons introduces a large number of graphene edges. These edges are highly reactive and thus attract many impurities. Doping graphene introduces defects into the lattice of the graphene interrupting the 2DEG. Finally the substrate can have phonons and charge trapping that interferes with the graphene. All of these significantly lower the carrier mobility of the graphene and detract from the device performance.

Another astounding property of graphene is the constant 2.3% light absorption in the visible light range. Because of this graphene has been looked at in various photonic applications. The 2.3% absorption arises due to graphene’s unique band structure which was already covered (Fig. 5). Fig. 6 shows several electron transitions in the graphene band structure. For intraband transitions the electrons absorbs a lower energy photon. The electron makes a transition from a lower energy state to a higher energy state in the conduction band. In the mid-IR range there is no absorption due to the Pauli blocking effect. As the phonon energy becomes larger than $2E_F$ absorption begins to occure again due to interband transitions at 2.3%. From this it can be seen that the absorption of graphene or optical conductivity can be tuned by adjusting the fermi energy ($E_F$) level through doping. This has lead to applications in graphene plasmonics which will be discussed in detail in chapter 4.
There are several ways to produce graphene. The first is mechanical exfoliation as mentioned previously. In this process HOPG is mechanically cleaved using tape. The graphite is continually thinned down by sticking the tape to itself until a few flakes of graphite remain. This is then stuck to the substrate and the tape is removed using a solvent (Fig 7). This method produces the purest form of graphene with the fewest defects or grains but it is only able to produce flakes in a few 10s of micrometer size. Because of the unreliability of this method it makes large scale manufacturing extremely expensive and virtually impossible.

Other manufacturing methods include epitaxial growth of graphene from silicon carbide substrates (Fig. 8). Using this method the SiC substrate is heated and the Si sublimes leaving the carbon surface. The carbon then reorders itself to form the graphene layer. This usually nucleates at a step or terrace in the substrate. Graphene grown on SiC is usually multi-layer due to the difficult control of growth.

Chemical vapor deposition (CVD) onto metal substrates has been one of the most promising techniques of graphene fabrication and is done by flowing H$_2$, CH$_4$, and Ar into a heated furnace onto a catalytic transition metal such as Cu or Ni (Fig. 9). This
Figure 7: Graphene exfoliation done using the scotch tape method. The graphite flakes can be seen on the scotch tape.[22]

Figure 8: Graphene grown directly from SiC substrate. [23]

Figure 9: Chemical Vapor Deposition of graphene onto a metal substrate.
method has demonstrated the ability to grow large areas of continuous mono-layer graphene. Because the graphene is grown onto a metal substrate, the graphene must be transferred onto a non-conducting substrate. This is usually done by coating the graphene with some polymer, typically poly(methyl methacrylate) (PMMA). Once coated the metal substrate is removed by wet etching then the graphene/PMMA layer is picked up by the desired substrate and the PMMA is removed (Fig. 10). Although this method produces the largest single-layer graphene it does have its drawbacks such as grain boundaries which disrupt the charge transport. The transfer process also introduces impurities and dopants into the graphene from the metal etching solution and PMMA. Even though CVD graphene has these issues it is still favorable for electronic devices due to the inexpensive and continuous growth. This dissertation will focus on CVD graphene.
1.3 Graphene Characterization

Due to the excitement that 2D materials has brought about, characterization techniques have been utilized to further investigate them. A few of these include scanning electron microscopy (SEM), scanning probe microscopy (SPM), Hall, and Raman spectroscopy.

Traditional optical microscopes work on the principal that the light coming from a surface can be refracted by a series of lenses allowing the magnification of that surface (Fig. 11). The resolving power of the optical power is not unlimited however but is described by the Abbe diffraction limit.

$$ R = \frac{\lambda}{n} \sin (\alpha) $$

Where $R$ is the resolution, $\lambda$ is the wavelength of the light, $n$ is the refractive index between the sample and the lens, and $\alpha$ is the angular aperture. It can be clearly seen that the major limiting factor in the resolution is the wavelength. For visible light the wavelength is in the range of 400-700 nm thus the resolution for an optical microscope...
would be around 250 μm. To further increase the resolution of microscopes the SEM was developed in 1937 by Manfred von Ardenne. The SEM works much the same way as a optical microscope but instead of using light as the source it uses electrons. The electrons from the source are accelerated by the anode. A series of magnetic lenses focus the beam and the scanning coils raster scan the beam across the surface of the sample. The backscattered electrons are then detected. The wavelength of an electron is dependent on its accelerating voltage \( \lambda = \frac{1.23}{\sqrt{v_a}} \). The typical wavelength of an electron with an accelerating voltage of 30kV is 0.007 nm, 4 orders smaller than that of visible light. The resolution of the SEM is on the order of 0.1 nm mainly due to aberrations in the magnetic lenses.

Due to the SEM using electrons for the beam there is a requirement that the sample be conductive or charging of the sample will occur leading to imaging faults. Along with this the electrons can burn through thin samples. This is a major problem for 2D materials since they are only single atom thick. The SEM can also only image samples and cannot characterize electrical properties or obtain true 3D images.

To overcome the weaknesses of SEM, the scanning tunneling microscope (STM) was developed in 1981 by G. Binning and H. Rohrer [27]. The STM uses the principle of quantum tunneling. In classical physics an electron can only cross a potential barrier by obtaining enough energy to go over the barrier, if there is not enough energy the electron will reflect back. For the case of quantum physics an electron has a certain probability of passing through the barrier provided the barrier is thin enough (Fig. 12). The tunneling current \( J_T \) has been shown to change by an order of magnitude for a 1 Å change in the distance between the tip and sample and is given by

\[
J_T \propto e^{-A\sqrt{\varphi s}}
\]

where \( A \) is a constant and is defined by \( A = \sqrt{(4\pi/\hbar)2m} \), \( m \) is the free-electron mass, \( \varphi \) is the average height of the barrier, and \( s \) is the barrier width. From Eq.
4 it can be seen that as the barrier width increases, the tunneling current decreases exponentially. In STM (Fig. 13) a voltage is applied between a tip (usually small gauge wire) and the sample. The tip is held a few angstroms away from the sample and scanned across the sample. The tunneling current is then measured. Due to the tunneling current sensitivity, the STM is the only variation of SPM that can achieve true atomic spatial resolution. The STM can be operated in two different modes. The first is constant height mode, where the tip is held to a constant height and the tunneling current varies as a function of the distance between the sample and the tip. The second is constant current mode where the height of the tip is adjusted during the scan to maintain a constant current. A few of the drawbacks to STM is the requirement for a conductive sample due to the electrons having to conduct from the tip to the sample. The second is that the conductivity of the sample cannot vary from point to point. If the sample has various conductivity values the tunneling current will change based on the change in conductivity and the topography of the sample will not be isolated from the change in conductivity.

Atomic force microscope (AFM) was developed in 1986 [30]. The AFM is part of
the SPM family. It consists of a cantilever with a tip attached to the end. A laser reflects off of the cantilever into a photo detector (Fig. 14). As the tip is scanned across the sample the cantilever bends according to the topography of the sample and the lasers reflection moves in the photo detector. In this way a true 3D image of the sample can be obtained. The AFM is able to obtain a lateral resolution of a few nanometers (based on tip diameter) and down to 1Å vertical resolution. The AFM has three main modes of operation, non-contact, tapping, and contact. In non-
contact mode the tip is hovered above the surface of the sample. In this case the attractive van der Waals forces attract the tip toward the sample surface. In tapping mode the AFM cantilever is vibrated so the tip is in intermittent contact with the sample. This is used if the sample is fragile or the objects of interest on the sample can be moved. The most widely used AFM mode is contact mode. In this mode the tip is lowered down and brought into contact with the sample using the repulsive, short range coulomb forces. This mode has two types of operation, constant height mode where the cantilever is held at a constant vertical position and must bend with the topography of the sample. The second is constant force contact mode in which as the tip is scanned across the sample the piezo crystal maintains a constant force at the tip on the sample or a constant location of the laser in the photodetector. This allows for a much larger vertical measurement distance than in constant height mode. The AFM has many setups that can analyzed different material properties of samples including electrical, magnetic, and physical properties. Some of these modes are used to measure electrical properties of materials are current sensing atomic force microscopy (CSAFM), Kelvin force microscopy (KFM), and scanning capacitance microscopy (SCM). CSAFM (Fig. 15a) which uses a DC voltage is applied between the tip and the sample. This allows for the AFM to sense current that may flow through the sample using a DC voltage. KFM (Fig. 15b) is done in tapping mode at a specific frequency. There is also an AC voltage applied between the tip and the sample at a separate frequency from the tapping frequency. The tip to sample voltage

Figure 15: CSAMF (a), KFM (b), and SCM (c) diagrams [33, 40, 34].
change produced a change in the electrostatic force between the tip and the sample making the cantilever oscillate at that frequency allowing the work function of the sample to be measured. SCM (Fig. 15c) uses an AC voltage between the tip and a semiconductor sample with a dielectric in between. The tip is brought into contact with the dielectric and the capacitance can be measured. This method is used for qualitative measurements of the doping profile for semiconductors.

Recently a new mode of AFM has been developed, Scanning Microwave Microscopy (SMM) (Fig. 16). SMM uses a conductive AFM cantilever that is connected to a network analyzer by a half wavelength coaxial resonator with a shunt 50 \( \Omega \) resistor. Our system is comprised of an Agilent 5420 AFM connected to an Agilent performance network analyzer (PNA) N5230C. The SMM uses the cantilever and tip of the AFM as a transmission line to propagate the radio frequency (RF) signal to the sample. The network analyzer, setup for single port measurements, then measures the complex reflection coefficient. From this reflected signal the electric properties of the material are able to be extracted. Since the SMM tip is considered to be an open transmission line, a shunt 50 \( \Omega \) resistor brings the tip and the coaxial resonator close
to matching the impedance of the network analyzer (50 Ω), significantly increasing the sensitivity. In this way the SMM is able to collect the complex reflection coefficient simultaneous with but independent of the topography measurement. Furthermore a traditional transmission line needs both a signal and a ground line to propagate the electric field. Because the AFM tip is used (Fig. 18) the ground is not available for the length of the probe. This problem is mitigated due to the size of the probe compared to that of the coaxial resonator. Due to the small size of the cantilever the electric field is still able to propagate down the ungrounded transmission line (Fig. 19). From here it can be seen that if both the signal and ground lines are equal in size the electric field is evenly distributed between the two. However if the signal line is much smaller than the ground line the electric field will only propagate along the signal line. This is the same in the SMM system. Because the AFM cantilever is much smaller (~100 nm) than the coaxial resonator (~300 μm) the electric field will continue to propagate down the cantilever even though the ground is far away.

The SMM is the only measurement system that is able to measure the reflection...
Figure 18: Dimensions of the SMM probe including an ungrounded transmission line and cantilever of length 2.1mm and 0.5mm respectively, a tip length of 90 - 150nm, and a tip diameter of 30 - 50 nm.

Figure 19: Transmission line electric field propagation for a transmission line with an equal size signal and ground (top), and a transmission line with a much smaller signal than ground (bottom).
coefficient with nm scale spatial resolution. Using this, both the conductivity and relative permittivity of a sample can be qualitatively analyzed. Recently a few attempts have been made to obtain a qualitative calibration of the SMM system [36, 37]. These attempts include an approach calibration by which the stray capacitance of the tip and cantilever were calibrated out of the system. This method requires the SMM tip be calibrated on the various materials that will be measured such as SiO$_2$ and heavily doped Si. This presents a significant problem however if the material has a complicated and unknown distribution. In this case it may be nearly impossible to setup the calibration on all of the different locations. The second method calibrates the capacitance using various sized Au pads. The capacitance of the Au pad is translated into the amplitude values of the complex reflection coefficient. From here a semiconductor sample with a thin oxide layer can be measured and the doping density can be extracted from the measurements. These methods however do not take into account what happens at various frequencies of the system and rely on knowing what the sample material is before measurements are performed to obtain accurate values. It has also been demonstrated that there are significant differences in both the half and quarter wavelength measurements [41, 38, 96]. These show that by contrasting the half and quarter wavelength frequency measurements a qualitative analysis of the conductivity of materials can be obtained. This will have a significant impact on the calibration of the SMM to obtain the half and quarter wave frequencies which has not been taken into account at this time.

Along with calibration, various experiments have been performed on graphene [38, 39]. Because the electric field of the SMM tip does not penetrate deeply into the sample SMM is an ideal technique to study the electrical properties of 2D materials. These papers take measurements of various graphene samples including single layer, multi layer, and graphene defects. This shows that SMM has height sensitivity when measuring graphene and can help analyze the features of graphene.
To date SMM has not been understood as a system. This dissertation will look at various analytical and numerical models and SMM measurements on various samples in an attempt to further the understanding of the SMM system. Here we present systematic results of numerical simulations performed using Keysight’s commercially available EMPro software showing several strong correlations between the conductivity and permittivity of different materials vs. the frequency at which the measurements are obtained and the SMM dimensions. This leads to an in depth understanding of materials electrical properties including CVD graphene and its defects and the newly developed spin-spray ferrite material.

2 Nano-Probe Electromagnetic Simulations

2.1 Analytical Analysis of the Electric Field Distribution for SMM

An analytical model was developed to describe the electric field distribution for the SMM. This was modeled as a vertical electric dipole above a layered medium (Fig. 20 [43]).

For this we must start with the electromagnet field to be \[ E_e + E_m \] \[ H_e + H_m \]

Where the electric and magnetic fields have been split into the electric field and the magnetic field due to the electric and magnetic components (subscripts e and m respectively). Then using Maxwell’s equations we get

\[ E = E_e + E_m \] \[ H = H_e + H_m \]
Figure 20: Model of SMM as a vertical electric dipole above a layered medium [43].
\[ \nabla \times \mathbf{E}_e = -j\omega \mu \mathbf{H}_e \]  
(7)

\[ \nabla \times \mathbf{H}_e = j\omega \varepsilon \mathbf{E}_e + \mathbf{J} \]  
(8)

\[ \nabla \times \mathbf{E}_m = -j\omega \mu \mathbf{H}_m - \mathbf{M} \]  
(9)

\[ \nabla \times \mathbf{H}_m = j\omega \varepsilon \mathbf{E}_m \]  
(10)

Solving the Maxwell’s equations we see that the total electric and magnetic fields then look like

\[ \mathbf{E} = \mathbf{E}_e + \mathbf{E}_m = -j\omega \mathbf{A} + \frac{1}{j\omega \mu \varepsilon} \nabla (\nabla \cdot \mathbf{A}) - \frac{1}{\varepsilon} \left( \nabla \times \mathbf{F} \right) \]  
(11)

\[ \mathbf{H} = \mathbf{H}_e + \mathbf{H}_m = -j\omega \mathbf{F} + \frac{1}{j\omega \mu \varepsilon} \nabla (\nabla \cdot \mathbf{F}) + \frac{1}{\mu} \left( \nabla \times \mathbf{A} \right) \]  
(12)

Using \( G \left( r, r' \right) \) (Green’s function), the fundamental solution to a point source, the solution for the free-space scalar Green’s function is well known and is

\[ G \left( r, r' \right) = \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{4\pi |\mathbf{r} - \mathbf{r}'|} \]  
(13)

Using this result we can now solve for the magnetic and electric potential

\[ \mathbf{A} \left( \mathbf{r} \right) = \frac{\mu}{4\pi} \iiint J \left( \mathbf{r}' \right) \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} dV' \]  
(14)

\[ \mathbf{F} \left( \mathbf{r} \right) = \frac{\varepsilon}{4\pi} \iiint M \left( \mathbf{r}' \right) \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} dV' \]  
(15)

Substituting Eqs. 14 and 15 in Eq. 11 and 12 and simplifying we get
\[
E(\mathbf{r}) = -j\omega \mu \iiint_V \left[ G_0(\mathbf{r}, \mathbf{r}') \mathbf{J}(\mathbf{r}') + \frac{1}{k^2} \nabla \nabla G_0(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}(\mathbf{r}') \right] dV' 
\]

\[
- \iiint_V \nabla G_0(\mathbf{r}, \mathbf{r}') \times \mathbf{M}(\mathbf{r}') \, dV' 
\]

(16)

From here if we look only in the z direction this will simplify to

\[
E_z(r) = -j\omega \mu_0 \left( 1 + \frac{1}{k_0^2} \frac{\partial^2}{\partial z^2} \right) \frac{e^{-jkror}}{4\pi r} 
\]

(17)

If we make the substitution

\[
e^{-jkr} \frac{r}{k} = \int_0^\infty \frac{k_\rho}{j k_z} J_0(k_\rho |\rho|) e^{-jkz} dk_\rho
\]

(18)

we get

\[
E_z(r) = \frac{1}{4\pi \omega \varepsilon_0} \int_0^\infty \frac{k_\rho^2}{j k_{z,0}} J'_0(k_\rho \rho) e^{-jk_{z,0} z} dk_\rho
\]

(19)

If we show this with the electric field reflecting off of the surface below we get

\[
E_z(r) = \frac{1}{4\pi \omega \varepsilon_0} \int_0^\infty \frac{k_\rho^3}{j k_{z,0}} J_0(k_\rho \rho) R_E e^{-jk_{z,0} z} dk_\rho
\]

(20)

\[
R_E^{(i)} = \frac{\varepsilon_i k_{z,i-1} e^{jk_{z,i} z_i} + B^{(i)} e^{-jk_{z,i} z_i}}{\varepsilon_i k_{z,i} e^{jk_{z,i} z_i} - B^{(i)} e^{-jk_{z,i} z_i}}
\]

(21)

\[
\frac{B^{(i-1)}}{A^{(i-1)}} = \frac{R_E^{(i)} - 1}{R_E^{(i)} + 1} e^{2k_{z,i-1} z_i}
\]

(22)

Using these equations MatLab was used to view the electric field distribution of the single dipole at various distances away from the substrate. Fig. 21 left shows a strong confinement of electric field at the single dipole that weakens as it is moved.
Figure 21: MatLab calculations and EMPro simulations for E-field distribution vs tip distance from substrate (left) and E-field maximum intensity vs permittivity (right).

Figure 22: Model of the tip of the SMM with a short cantilever for E-field distribution simulations.

Away from the substrate. Along with changing the tip distance from the substrate, the relative permittivity was changed while maintaining the tip distance (Fig. 21 right). The simulation shows that as the relative permittivity increases, the electric field at the tip also increases.

### 2.2 Numerical Simulations of SMM

To confirm the analytical results, measurements in Fig. 21 were simulated in the commercially available Keysight Technologies EMPro software (Fig. 22).

In this model the cantilever and tip were made of a perfect electrical conductor (PEC), the substrate was a thin layer (10 nm) of SiO$_2$ on top of a thick layer (10
μm) of Si, and the ground plane on the back of the substrate was a layer of PEC. The tip narrows to a 100 nm point with a rounded end. A 50 Ω supply was shunted from the ground plane to the end of the cantilever. The simulation was done using finite element method (FEM). The meshing was performed automatically by the software using a tetrahedral mesh. EMPro performs an automatic mesh study for every FEM simulation by comparing the S-parameters from one run to the next. For this simulation a delta error of 0.001 was chosen over two consecutive passes to verify convergence of the mesh. For this simulation a constant relative permittivity of 3.9 for the sample was used. From Fig. 23 it can be seen that the electric field is heavily concentrated at the tip. Figure 21 shows that as the tip moves away from the sample the E-field decreases quickly at first and then reaches an asymptote. Also from this figure it can be seen that as the permittivity increases the E-field increases. For this measurement a distance of 50 nm was maintained. Both the analytical (MatLab) and numerical (EMPro) results show the same trend of increasing E-field for decreasing tip to sample distance. The values of the EMPro simulations are several orders of magnitude lower than the analytical model. This is due to the analytical model being modeled as a point source and the numerical model having a 100 nm tip diameter. Because the numerical model has a much larger tip diameter the E-field has a lower confinement and thus is much weaker than the analytical model. This however confirms that the numerical simulation is correct and can be used to further investigate the SMM system.

This simulation was further analyzed by bringing the SMM tip in contact with a circular Au pad on top of a SiO$_2$ substrate with Au on the bottom (Fig. 24). Using this setup the capacitance of various sizes of Au pads were measured and compared to the calculated values for capacitance (Table 1). From Fig. 24 it can be seen that there is large parasitic capacitance that needs to be accounted for. This was done by removing the Au pad and simulating only the substrate and cantilever/tip. This was
Figure 23: Electric field at the tip of the cantilever.

Figure 24: Keysight EMPro model of SMM tip with Au pad (top) and e-field distribution (bottom) showing stray capacitance due to the cantilever.

Table 1: SMM Capacitance Measurements

<table>
<thead>
<tr>
<th>Disk Diameter (µm)</th>
<th>Simulated Capacitance (fF)</th>
<th>Calculated Capacitance (fF)</th>
<th>Percnet Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-Embedding</td>
<td>11.2</td>
<td>nA</td>
<td>nA</td>
</tr>
<tr>
<td>10</td>
<td>28.9</td>
<td>27.1</td>
<td>7%</td>
</tr>
<tr>
<td>6</td>
<td>10.5</td>
<td>9.8</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>1.25</td>
<td>1.08</td>
<td>15%</td>
</tr>
<tr>
<td>1</td>
<td>0.32</td>
<td>0.27</td>
<td>18%</td>
</tr>
</tbody>
</table>
used as the de-embedding structure. For each of the results presented in Table 1 the
de-embedding capacitance value was subtracted from the results with the capacitor
and cantilever leaving only the capacitance of the Au pad. Table 1 show the simulated
vs. analytical capacitance with error between them. The analytical capacitance was
calculated using the formula
\[
C = \varepsilon_r \varepsilon_0 \frac{\pi (\frac{d}{2})^2}{t}
\]
where \(d\) is the diameter of the disk and \(t\) is the thickness of the dielectric between the
base and the disk which is 100 nm. It can be seen that the difference between the
simulated values and analytical values are very close (~10%). As the disk diameter
decreases the percent of the error increases. This can be attributed to the fringe
effects of the capacitance not being taken into account for the analytical capacitance
calculations.

A more detailed model was constructed to study the SMM as a system. The model
consists of a 3.0 cm long coaxial resonator with 50 ohm characteristic impedance, a
shunt 50 ohm resistor at one end of the resonator, a cantilever, and a tip of the AFM
at the other end (Fig. 25b). The tip is formed as a cone with a base diameter of 100
\(\mu\)m and an end diameter of 100 nm. The sample was a \(300 \times 300 \times 200 \mu m^3\) block with
the tip placed at the top center. The magnitude and the phase of \(\Gamma_m\) (the complex
reflection coefficient) were computed versus frequency (Fig. 26 b-d) in a vacuum by
taking the electrical conductivity \(\sigma = 0\) S/m and the relative permittivity \(\varepsilon_r = 1\)
for the sample and compared to the measurements (Fig. 26 a). This shows that for
the half wavelength the amplitude approaches a matching impedance and the phase
approaches ±90 degrees and for the quarter wavelength the amplitude approaches 0
with a phase of ±180 degrees. Various thicknesses of the coaxial resonator dielectric
was used, specifically 209 \(\mu m\), 304 \(\mu m\), and 836 \(\mu m\). It was found that the dielectric
thickness has a profound change on both the amplitude and phase measurements (Fig.
27). The change in the amplitude and phase are believed to depend on the electric
Figure 25: SMM Simulation of SMM probe with half wavelength coaxial resonator.

Figure 26: EMPro simulation and measured frequency sweep of the complex reflection coefficient. Both the experimental (a) and simulated (b) magnitude and simulated amplitude (c) phase (d) are shown. The quarter (16.5 and 18.3 GHz) and half (17.5 and 19.2 GHz) wavelength frequencies can be clearly seen.
field strength at the tip of the SMM compared to that of the rest of the system. As the dielectric thickness decreases the electric field within the coaxial cable begins to dominate the system and the tip is no longer the dominate part (Fig 28). The dielectric thickness of the actual SMM system is 304 μm which, as can be seen in Fig. 27, leads to a decreasing amplitude and an increasing phase for an increase in conductivity of the sample according to the simulation. This is contrary to what we have obtained in the measurements. This is due to the tip in the model having a 100 nm diameter (limited by the meshing capabilities) and the tip in the system having a 10 nm diameter. As the tip diameter decreases the electric field enhancement increases and the tip electric field is dominant. However because of the nanometer scale size of the tip and the centimeter scale size of the coaxial resonator are coupled together in this simulation it was not possible to make the tip size any smaller than 100 nm due to meshing constraints without causing the software to crash. To overcome this limitation, instead of making the tip smaller, the dielectric thickness for the coaxial
resonator was increased to 836 μm and, as can be seen in Fig. 28, allows for the electric field of the tip to dominate the system. The dielectric thickness that was chosen for the rest of the simulations is 836 μm. Figure 29 shows that for the half wavelength an increase in conductivity leads to an increase in the amplitude but a decrease for the phase. For the quarter wavelength an increase in conductivity leads to a decrease in both the amplitude and phase. This is in agreement with the experimental results that will be shown in Chapter 3. The resonant frequency of the SMM can be changed by increasing or decreasing the length of the coaxial resonator. For these simulations a length of 3 cm was chosen and as shown in Fig. 26, the seventh $\frac{\lambda}{2}$ and $\frac{3}{4}$ resonances appeared at 17.3 GHz and 16.2 GHz with the phase 90° and 180°, respectively. This is in agreement with the circuit model in Fig. 25. Figure 30 shows the change of the amplitude and the phase of the $\Gamma_{in}$ by varying relative permittivity at $\frac{\lambda}{2}$ and $\frac{3}{4}$ resonant frequencies for a number of materials with different electric conductivities. In detail the conductivity was chosen to be 0 Ω cm for the SiO$_2$, 0.16 Ω cm for the Si, 1.2 × 10$^{-4}$ Ω cm for the CVDG, and 2.0 × 10$^{-8}$ Ω cm for the Au. In the calculations, SiO$_2$ has been chosen to serve as the reference. As reported in Refs [71] and [72], the sheet resistance of CVD-grown graphene varies
Figure 29: EMPro simulation of amplitude and phase vs. conductivity for half and quarter wavelength. Various permittivity values were used to correspond to several materials including SiO$_2$, Si, Au, and graphene.

Figure 30: Numerical EMPro simulation of half wavelength amplitude and phase (a) and quarter wavelength amplitude and phase (b) vs. relative permittivity for CVDG normalized to SiO$_2$. The simulated values are also shown for the magnitude and phase of Au for both the half and quarter wavelength case. It can be seen that for the half wavelength case the Au has a higher magnitude than the CVDG and for the quarter wavelength case a lower magnitude showing that Au has a higher conductivity than Au and the CVDG has a high relative permittivity.
from $3.0 \ \Omega/\square$ to $2000 \ \Omega/\square$, and the relative permittivity is less than $2 \times 10^5$ above 6.0 GHz. Comparing to the SiO$_2$ reference, graphene shows a larger amplitude but a smaller phase angle of the $\Gamma_{in}$ at the $\frac{\lambda}{2}$ resonance, and a smaller amplitude and phase angle of the $\Gamma_{in}$ at $\frac{\lambda}{4}$ resonance. The changes of the $\Gamma_{in}$ for both the amplitude and the phase are rather small as the relative permittivity varies from $0 - 2 \times 10^5$ ($\Delta|\Gamma| \sim 0.03 \text{ dB}, \Delta\vartheta \sim 0.6^\circ$ for half and $\Delta|\Gamma| \sim 0.00005 \text{ dB}, \Delta\vartheta \sim 0.006^\circ$ for quarter). Thus the difference of the $\Gamma_{in}$ for changes in the electrical conductivity between the graphene and the SiO$_2$ ($\Delta|\Gamma| \sim 3.94 \text{ dB}, \Delta\vartheta \sim -8.95^\circ$ for half and $\Delta|\Gamma| \sim -0.008 \text{ dB}, \Delta\vartheta \sim -0.006^\circ$ for quarter) is the dominant reason for the change of the $\Gamma_{in}$ at both the $\frac{\lambda}{2}$ and $\frac{\lambda}{4}$ resonances. In addition, it should be pointed out that the change of the $\Gamma_{in}$ at $\frac{\lambda}{2}$ resonance is always larger than those calculated at $\frac{\lambda}{4}$ resonance. This is due to $\Gamma_{in}$ at half wavelength being much closer to a matching network than that of the quarter wavelength frequencies.

3 Characterization of Graphene

3.1 Introduction

Since experimentally isolated in 2004 [75], graphene, a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, has revealed various astonishing properties [75-80] and found broad potential applications in electronics such as field effect transistors (FETs) [75, 81-85], memories [86, 87], and sensors [81, 88]. Its electron mobility was reported up to $\sim 200,000 \ cm^2/V/s$ [80], rendering tremendous promises in radio frequency (RF)/microwave (MW)/terahertz (THz) electronics. Though the zero energy band-gap impedes it from logic device due to the low on/off current ratio, graphene is considered as an excellent candidate for RF/MW/THz applications where the need for large on/off current ratio is not compulsory [89-94]. A transistor built on exfoliated graphene has demonstrated a 300 GHz cut-off frequency
in 2010 [89]. Based on the transit time measurement, the highest cutoff frequency was projected to 1.4 THz [90]. However, the incapable of scalability and reproducibility prevents the mechanical exfoliation from the main stream semiconductor industry. The alternative is chemical vapor deposition (CVD) of large scale graphene sheets. The main obstacle of CVD-grown graphene sheets is the low electrical conductivity which strongly depends on the growth and processing conditions. Understanding of the correlation between the structural- and electrical- properties becomes indispensable to perfect the CVD-grown graphene, which requires in-situ characterization of the electrical properties at RF/MW frequencies. Most of the electrical characterization of graphene sheets has been carried out at DC such as contact mode atomic force microscope, scanning probe station, and hall measurements. Due to the monolayer feature of graphene, these methods suffer significantly from the large and uncontrollable contact resistance. Recently, the electrical properties of a multiple-layer graphene sheets have been characterized by using a coplanar waveguide, showing a strong frequency dependent complex electrical permittivity at frequency below 4 GHz, while almost frequency independent above 4 GHz. Below 4 GHz, the real and imaginary parts of the relative complex permittivity of graphene exceed $10^4$. Moreover, conductivity mapping of monolayer graphene has been obtained using the so-called near field scanning microwave microscope (SMM) at RF/MW frequency with a spatial resolution of better than 100 nm. The enhanced tip-sample capacitive coupling at RF/MW frequency allows the method to minimize the impact by the contact resistance. In this paper, systematic in situ measurements have been performed using SMM to characterize monolayer CVD-grown graphene sheets. Correlation between the contrast of the amplitude and phase of the reflection coefficient and the frequencies is established and investigated. By comparing the contrast differences of graphene and the reference samples recorded at half- and quarter- wavelengths resonances, the conductivity and permittivity of the graphene sheets at RF/MW frequencies can be qualitatively
Table 2: Substrates and Resistivities (Ω cm)

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>DLG</th>
<th>SLG</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 × 10^{-8}</td>
<td>0.5 × 10^{-4}</td>
<td>1.2 × 10^{-4}</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

determined. Along with electrical properties of pristene graphene, graphene with defects were characterized. These defects include point defects from bombardment with an oxygen plasma etcher and wrinkles in the graphene. Defects in graphene have been used as a way to fictionalize the graphene as well as a method of opening up a bandgap. Here we show that by introducing different densities of point defects into the graphene the conductivity varies accordingly. We also show a connection between the conductivity of graphene and graphene wrinkles.

### 3.2 Experiment

For the graphene chemical vapor deposited graphene (CVDG) foils were purchased from Graphene Supermarket. The graphene sheets were deposited on both sides of the copper substrate, forming a CVDG/Copper(20μm)/CVDG stack. To keep the structural and electrical properties of the graphene sheets identical, a single atomic layer CVDG was used in this work. The number of graphene layers has been verified by Raman spectrum. The CVDG sheet was transferred from the as-grown copper foil to a variety of substrates including a silicon wafer covered by a 300 nm thick thermal oxide layer (sample A), a bare silicon wafer (sample B), a silicon wafer covered by a 300 nm thick thermal oxide layer and 100 nm thick gold layer (sample C), and a silicon wafer covered by a 300 nm thick thermal oxide layer and a CVDG sheet (sample D) (see Table 2). In details, after coating 200 nm thick PMMA on the front side of the CVDG/Copper/CVDG stack, the backside CVDG and the copper substrate were removed by oxygen plasma etching and Fe(NO₃)₃ wet chemical etching, respectively. Afterwards the PMMA/CVDG stack was placed in DI water to rinse and then removed with the desired substrate (DSUB). Post-heating to evaporate
the remaining DI water and to reflow the PMMA to release wrinkles that may be in the CVDG were performed before removing the PMMA in acetone to complete the substrate transferring and to form CVDG/DSUB stacks. The grating structure was defined by a photo mask in a coated AZ-5214 photoresist layer on the surface of the CVDG/DSUB stack using standard photolithography techniques, and then transferred to CVDG layer by oxygen plasma etching. The CVDG width was 4 µm with a spacing of 6 µm. The photoresist was removed using an acetone/IPA rinse. For the CVDG on CVDG sample, for the double layer graphene (DLG), a piece of graphene was patterned with gratings while still on the Cu substrate using the above photolithography procedure. The photoresist (PR) was then removed and the patterned CVDG/Cu stack was spin coated with PMMA. These samples were then etched and transferred onto a SiO₂/CVDG substrate. In this way we obtained a pattern of SLG and DLG gratings. The graphene was verified before and after fabrication by Raman spectroscopy to verify that the fabrication methods did not lead to any significant defects in the graphene. Hall measurements were taken of the CVDG after the transfer process which show a sheet resistance of around 1200 Ω/□.

Four other samples were fabricated to investigate defects in graphene. After the PR was patterned the samples were oxygen plasma etched at 2 watts for 10 seconds, 5 watts for 10 seconds, 20 seconds, and 30 seconds (samples E, F, G, and H respectively). The PR was then removed.

A freshly transferred sheet of graphene on SiO₂ was used as the sample for the graphene wrinkle measurements. The transfer method described leaves wrinkles and defects in the graphene that can be found using AFM.

The samples were characterized using Scanning Microwave Microscopy (SMM) consisting of an Agilent 5420 AFM with the tip connected to an Agilent performance network analyzer (PNA) N5230C. As reported in our previous work [96], such a system is capable of obtaining both the surface topography of the sample and the reflected
complex scattering parameters \((s\text{-parameter})\) between 1.0 - 20.0 GHz simultaneously without dependence on each other. The AFM-tip is connected to the PNA via a 1.5m coaxial cable connected to a 24 cm coaxial cable connected to the transmission line resonator (TrLR) as shown in Fig. (25a), close to the configuration presented in Refs [30] and [36]. By varying the operating frequency, the TrLR resonates at a series of frequencies when the length of the TrLR equals to integer multiples of half-\((\lambda/2)\) and quarter-\((\lambda/4)\) wavelength. The length of the TrLR is about 3.0 cm and is designed to have \(\lambda/2\) resonance in the vicinity of 2.5 GHz. From the equivalent microwave circuits (Fig. (25c-e)), \(\Gamma_{\text{in}}\) reveals mostly the characteristic of the load admittance \(y_L\) at \(\lambda/2\) resonance, while the load impedance \(z_L\) at \(\lambda/4\) resonance. The normalized complex load admittance \(y_L = g_L + j b_L\) reflects the tip-sample interaction, where the normalized conductance \(g_L\) represents the conductive loss and the normalized susceptance \(b_L\) represents the capacitive coupling at the end of the tip. After shunting a normalized resistor in Fig. 25 (c), the phase of \(\Gamma_{\text{in}}\) approaches to \(\pm \pi/2\) at \(\lambda/2\) resonance and 0 or \(\pi\) at \(\lambda/4\) resonance. This will be used as the criterion in experiments to identify the \(\lambda/2\) and \(\lambda/4\) resonances. Prior to the measurements, the SMM system was calibrated from the 1.5 m coaxial cable to the PNA. This eliminated the resonant frequencies that arise due to the long cable. The \(\lambda/2\) and \(\lambda/4\) resonant frequencies were determined by rising the SMM tip to about 40 \(\mu\)m above the sample surface and then performing a frequency sweep (Fig. (26a)). The first \(\lambda/2\) resonance was measured at 2.3 GHz. In this work, a frequency of 18.3 GHz was chosen for the quarter wavelength and a frequency of 17.5 GHz was chosen for the half wavelength both of which correspond to the 7th harmonic. Afterwards the tip was lowered onto the sample and raster scanned across.
Figure 31: SMM Measurements of Half wavelength amplitude (a) and phase (b) measured at 17.5 GHz and quarter wavelength amplitude (c) and phase (d) measured at 18.3 GHz. The half wavelength amplitude image (a) show that the high conductivity graphene is brighter in contrast than the lower conductivity SiO\textsubscript{2} while the contrast of the phase profile (b) is reversed to that of the amplitude. In both the quarter wavelength amplitude (c) and phase (d) the graphene is darker than the SiO\textsubscript{2} substrate.

3.3 Results and Discussion

Images of amplitude and phase of $\Gamma_{in}$ at $\lambda/2$ and $\lambda/4$ resonances were measured using SMM (Fig. 31) on sample A, i.e. graphene grating on SiO\textsubscript{2}/Si substrate. Due to the nanometer-sized AFM tip, the RF field is highly concentrated at the end of the tip, thus the SMM measurements reflect mainly the electrical property of the surface of the sample. The $\Gamma_{in}$ exhibits a larger value of amplitude but a smaller phase angle reflected from graphene grating than from SiO\textsubscript{2}/Si at $\lambda/2$ resonance (Fig. 31a and b) which is in agreement with the EM simulations (Fig. 30a). At $\lambda/4$ resonance (Fig. 31c and d), the $\Gamma_{in}$ from graphene exhibits larger values of both the amplitude and phase than the substrate, which coincides well with the EM simulations (Fig. 30b). It is worth mentioning that the difference of the amplitude and phase between the graphene grating and the SiO\textsubscript{2}/Si substrate recorded at $\lambda/2$ resonance is more
Figure 32: Half wavelength (17.5 GHz) SMM amplitude and phase measurements for CVDG on Si (a, b), CVDG on Au (c, d), and CVDG on CVDG (e, f). The CVDG on Si follows the same contrast as that of CVDG on SiO$_2$ while the CVDG on Au is opposite. This is due to the Au having a higher conductivity than the CVDG. The CVDG on CVDG samples shows that the DLG is more conductive than the SLG.

than two orders higher for the amplitude and one order higher for the phase than those measured at $\lambda/4$ resonance. As revealed in the EM simulation, $\lambda/4$ resonance is less sensitive to the variation of the $\Gamma_{in}$ than $\lambda/2$ resonance. For this reason the following discussions are focused on the measurements at $\lambda/2$ resonance. The SMM measurements recorded at $\lambda/2$ resonance of samples B, C, and D are shown in figure 32. As in the measurements and simulations for CVDG on SiO$_2$/Si, the larger value of amplitude and the smaller phase angle of the $\Gamma_{in}$ from graphene in Fig. 32 (a-b) is the results of the higher conductivity of graphene than the silicon substrate. On the contrary, the graphene shows a smaller value of amplitude and a larger phase angle in Fig. 32 (c-d), manifests its lower electrical conductivity than gold. Coordinating the results from Fig. 32 (a-b) and 32 (c-d) turns out that the graphene possesses a conductivity higher than silicon but lower than gold. Fig. 32 (e-f) show the SMM measurements for CVDG gratings on CVDG (sample D). It can be seen that the
CVDG substrate is darker in contrast than the CVDG gratings. This is due to the SMM system measuring two layers of CVDG (DLG), the CVDG substrate and the CVDG gratings, when the tip is on the CVDG gratings and only measure one layer of CVDG (SLG) when the tip is on the substrate. The SLG and DLG have the same value of permittivity, thus the imaging contrast in Fig. 32 (e-f) is solely contributed by the resistance difference. The DLG can be considered as two SLG connected in parallel, leading to the reduction of the resistance. However due to the proximity of the conductivity between the SLG and DLG the contrast is very week compared to the other samples. This provides a method to qualitative determine the electric conductivity of graphene at RF by comparing with various substrates. Based on the simulations the permittivity of the graphene can also be estimated. The measurements (Fig 32 (c-d)) show that for the half wavelength amplitude the graphene is darker than the Au and for the half wavelength phase the graphene is brighter than the Au. From the simulations the only case at which the graphene is brighter than the Au for the half wavelength phase is when the relative permittivity of graphene is greater than $1 \times 10^5$. From this the measurements show that the CVDG has a value of $\varepsilon_r > 1 \times 10^5$ and is in agreement with [71].

The graphene defects are presented in Fig. 33 and 34. The $\lambda/2$ amplitude measurements for the graphene defects (Fig. 33) shows the pristine (un-etched) graphene as light bands and the etched graphene as dark bands while the $\lambda/2$ phase measurements (Fig. 34) show the un-etched graphene as dark bands and the etched graphene as light bands. Based off of this contrast the un-etched graphene is more conductive than the etched graphene. Furthermore the $\lambda/4$ measurements show both the amplitude (Fig. 35) and phase (Fig. 36) have dark bands for the un-etched graphene and light bands for the etched graphene, the same as the $\lambda/2$ phase. This further shows the conductivity of the un-etched graphene is larger than the etched graphene. These images also show that as the etching time and power is increased the conductivity of
Figure 33: Half wavelength (16.04 GHz) amplitude SMM measurements of oxygen plasma etched graphene gratings on a graphene substrate. The etching time and power was 2 watts for 10 seconds (a), 5 watts for 10 seconds (b), 5 watts for 20 seconds (c), and 5 watts for 30 seconds (d). The light areas represent the pristine (un-etched) graphene and have a higher conductivity while the dark areas represent the etched graphene and are less conductive.
Figure 34: Half wavelength (16.04 GHz) phase SMM measurements of oxygen plasma etched graphene gratings on a graphene substrate. The etching time and power was 2 watts for 10 seconds (a), 5 watts for 10 seconds (b), 5 watts for 20 seconds (c), and 5 watts for 30 seconds (d). The dark areas represent the pristine (un-etched) graphene and have a higher conductivity while the light areas represent the etched graphene and are less conductive.
Figure 35: Quarter wavelength (6.12 GHz) amplitude SMM measurements of oxygen plasma etched graphene gratings on a graphene substrate. The etching time and power was 2 watts for 10 seconds (a), 5 watts for 10 seconds (b), 5 watts for 20 seconds (c), and 5 watts for 30 seconds (d). The dark areas represent the pristine (un-etched) graphene and have a higher conductivity while the light areas represent the etched graphene and are less conductive.
Figure 36: Quarter wavelength (6.12 GHz) phase SMM measurements of oxygen plasma etched graphene gratings on a graphene substrate. The etching time and power was 2 watts for 10 seconds (a), 5 watts for 10 seconds (b), 5 watts for 20 seconds (c), and 5 watts for 30 seconds (d). The dark areas represent the pristine (un-etched) graphene and have a higher conductivity while the light areas represent the etched graphene and are less conductive.
Figure 37: Raman measurements of etched graphene for samples E, F, G, and H. These measurements show that as the etching time and power increases the defect peak increases and the 2D peak decreases showing that the defect density is increased.

the graphene decreases. Raman measurements were also taken of the same samples to verify the defect density of the etched graphene (Fig. 37). The Raman peaks from left to right are the D-peak, G-peak, and 2D-peak. The D-peak shows the amount of defects in the graphene, the G-peak shows the amount of carbon, and the 2D-peak shows the amount of 2D carbon (graphene) for the sample. Figure 37 shows that sample E has the least amount of etching as expected followed by sample F. From the Raman measurements, however, it appears that sample G has been etched more than sample H. Table 3 compares the SMM measurements to the Raman measurements. The first two rows show the change from etched to pristene graphene for the amplitude and phase of the $\lambda/2$ SMM measurements. These are compared to the Raman measurements and can be seen that as the D-peak increases the change in contrast also increases for the SMM measurements. This shows that as the defects in the graphene increase the conductivity of the graphene decreases. The D/G intensity
Table 3: SMM and Raman Measurement Comparison

<table>
<thead>
<tr>
<th></th>
<th>2W, 10s (E)</th>
<th>5W, 10s (F)</th>
<th>5W, 30s (H)</th>
<th>5W, 20s (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda/2) Amp (dB)</td>
<td>To Small</td>
<td>0.02075</td>
<td>0.55825</td>
<td>0.7575</td>
</tr>
<tr>
<td>(\lambda/2) Phase (deg)</td>
<td>To Small</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011425</td>
</tr>
<tr>
<td>Raman D</td>
<td>39.6</td>
<td>53</td>
<td>75</td>
<td>75.1</td>
</tr>
<tr>
<td>D/G</td>
<td>1.85</td>
<td>1.53</td>
<td>1.32</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Figure 38: SMM measurements of graphene wrinkles showing topography, half wavelength amplitude, and half wavelength phase.

...continues...

...continues...

Graphene wrinkles were also measured using SMM to characterize the conductivity values of the graphene wrinkles compared to the surrounding graphene (Fig. 38). This shows that, for the half wavelength measurements, the graphene wrinkles are less conductive than the surrounding graphene. Cross sections were obtained from the SMM measurements and shows two types of wrinkle structures, un-collapsed and collapsed (Fig 39). The cross section for the collapsed wrinkle shows a dip in the...
Figure 39: Graphene wrinkle cross sections showing collapsed (a, b, c) and un-collapsed (d, e, f) structures for topography (a, d), SMM $\lambda/2 |\Gamma|$ (b, e), and SMM $\lambda/2 \theta$.

Figure 40: Drawings of graphene wrinkle categories ripple (a), un-collapsed wrinkle (b), and collapsed wrinkle (c) [73].

center of the graphene and can be imagined as the graphene folding back on itself (Fig 40). The measurements clearly show the edges of the wrinkle where the graphene folds back onto itself. From the SMM measurements it can be seen that not only does the wrinkle have an overall lower conductivity than the surrounding graphene but that the edges of the wrinkles have a lower conductivity than the rest of the wrinkle. This could be from the charge density changes at the areas of the tightly curved graphene [74]. A number of graphene wrinkles were measured and a chart of the height vs. amplitude and phase were created (Fig. 41) the red marks show the measurements taken from the collapsed wrinkles while the other measurements were taken from the
Figure 41: Graphene wrinkles vs. SMM amplitude and phase showing that as the height of the wrinkle increases, the amplitude decreases and the phase increases leading to the conclusion that as the height of the wrinkle increases the conductivity of the wrinkle decreases. The red marks are from measurements taken from the collapsed wrinkles and the black marks are from the un-collapsed wrinkles.
Figure 42: SMM $\lambda/2$ amplitude and phase measurements across several un-collapsed wrinkles showing that the edges of the wrinkle (locations 1 and 3) are generally less conductive than the center of the wrinkle (location 2).

un-collapsed wrinkles and ripples. The measured wrinkles that are below 4 nm are believed to be ripples while the wrinkles that are taller than 4 nm are un-collapsed wrinkles. Further measurements were taken of the collapsed wrinkles (Fig. 42) to show that the edges are less conductive than the center of the wrinkle. This could be due to the edges having a tighter bend than the rest of the wrinkle and thus having a different charge density.

### 3.4 Conclusions

Imaging contrast in SMM measurements show strong frequency dependency of both the amplitude and phase of the reflection coefficient. Comprehensive understanding of the SMM image contrast requires correlative investigation of the measurements
at various frequencies. This work presents a method capable of qualitative determination of both the electric conductivity and relative permittivity of graphene at RF by correlating measurements performed at a series of harmonic resonances. This method is supported by three dimensional numerical electromagnetic simulations. Using the stated method, electrical characterization of 2D-materials at nanometer scale spatial resolution can be performed for the first time. These results could lead to breakthrough investigations of the electrical properties of nanomaterials that were previously unattainable.

The SMM measurements of graphene defects have been verified by Raman spectroscopy and show that as the defect levels in graphene increase, the conductivity of the graphene decrease. This is the first time that this has been observed on nano-scale resolution for graphene defects.

Various forms of graphene wrinkles and ripples have been measured by AFM and for the first time, using SMM measurements, the conductivity across graphene wrinkles has been observed. This agrees with the theoretical models that have been presented in other papers and could connect the change in charge density of graphene, due to the folding, with the conductivity.

4 Graphene Plasmonics for THz and IR Applications

4.1 Introduction

Graphene, with its near-ballistic transport at room temperature and high carrier mobility ranging between 3000 and 200,000 cm$^2$/Vs, has been studied extensively for its use as a potential material for nanoelectronics, especially for high-frequency applications. Recently much research has gone into plasmonics for applications in
communications and sensing. Plasmons are defined as the collective oscillation of a free electron gas (plasma). These oscillations have been used since the middle ages in applications such as stained glass windows however it has not been until recently ~1950’s that plasmons have been understood. As has already been stated plasmons were first observed in applications such as stained glass windows in which metal nano-particles (such as Au) gave the glass its vibrant colors when light was shined through it. This arises from the coupling of electromagnetic waves being coupled to the electrons of the nano-particle and creating an oscillation of the free electrons. This is known as the volume or bulk plasmon where the entire volume is in resonance at once and is defined from the equation of a free electron gas as follows.

\[
m \frac{d^2x}{dt^2} + m \gamma \frac{dx}{dt} + mQx = -eE
\]  

(24)

In Eq. 24 the first term is the force, the second term is the damping where \( \gamma = \frac{1}{\tau} \) and \( \tau \) is the mean free time of the electron. The third term is the restoring force due to the positive ions attracting the negative charged electron and will be ignored from here on because it is weak. The right side of the equation is the applied electric field. From here we can assume a solution of

\[
x(t) = x_0 e^{-i\omega t}
\]  

(25)

Using this to solve equation 10 we get

\[
x_0 = \frac{eE}{m (\omega^2 + i\gamma \omega)}
\]  

(26)

The macroscopic polarization is \( P = -nex_0 \) and the electric displacement field is \( D = \varepsilon (\omega,k) E = \varepsilon_0 E + P \). Substituting equation 26 into these we can get the complex permittivity of metal to be
\[ \varepsilon(\omega, k) = \varepsilon_0 - \frac{ne^2}{m(\omega^2 + i\gamma \omega)} \quad (27) \]

From equation 27 we can define the plasmonic frequency to be \( \omega_p = (ne^2/m\varepsilon_0)^{1/2} \) and the complex permittivity becomes

\[ \varepsilon(\omega, k) = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} \right) \quad (28) \]

From here we can define surface plasmon polaritons (SPP). SPP are sustained waves that occur at a metal/dielectric interface and stay close to the surface. The bulk wave dies out exponentially. We start with the Helmholtz equation to define surface waves at a metal dielectric interface as follows

\[ \Delta \mathbf{E} + k_0^2 \varepsilon(\omega) \mathbf{E} = 0, \quad (29) \]

\[ k_0 = \frac{\omega}{c} \quad (30) \]

\[ \mathbf{E}(\mathbf{r}) = \mathbf{E}_0 e^{i\beta z} \quad (31) \]

\[ \frac{\partial^2 \mathbf{E}(x)}{\partial x^2} + \left( k_0^2 \varepsilon(\omega) - \beta^2 \right) \mathbf{E} = 0 \quad (32) \]

From here we have the following boundary conditions and can solve for the dispersion curve.

\[ A_1 = A_2 \quad (33) \]

\[ \frac{k_1}{\varepsilon_1} A_1 = \frac{k_2}{\varepsilon_2} A_2 \quad (34) \]

\[ \beta = k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (35) \]

We can see from equation Eq. 27 that if we minimize the loss \( \gamma \) we can simplify
Figure 43: Kretschmann configuration (a) and grating configuration (b) to excite a surface plasmon at a metal/dielectric interface.

this equation to be

\[ \varepsilon(\omega, k) = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2} \right) \]  

(36)

Metals in the visible light range have a very large, negative real part of the permittivity and a small positive imaginary part of the permittivity. Because of the small imaginary part the losses are minimized in the visible light range. This fits the above case and is why metals are chosen for most plasmonic applications. This however is not good enough to launch a plasmon. If we model the surface plasmon momentum (Eq. 35) and the momentum of light in air (Eq. 30) we will see that the momentum of the light in air needs to be increased to achieve \( k_{sp} \approx k_i \), where \( k_i \) is the incident light on the metal. There are two main ways to achieve this increase in momentum. The first is to increase the momentum of the light through total internal reflection with a prism (Fig 43a). In this case the light completely reflects off of the bottom (metal side) of the prism which causes an evanescent wave. This evanescent wave gives us the extra momentum that is needed to create a surface plasmon and has the form

\[ k_{sp} = k_0 \sqrt{\varepsilon_d} \sin \theta \]  

(37)

where \( \theta \) is the angle of light coming into the prism. At certain values for this angle total absorption of the incident light occurs and the entire amount of light is
transformed into the surface plasmon.

The second way to achieve the extra momentum needed to launch a surface plasmon is using a diffraction grating (Fig. 43b). In this case the momentum takes the form of

\[ k_{sp} = k_0 \sin \theta \pm \frac{2\pi}{\Lambda} \]  

(38)

where \( \Lambda \) is the period of the grating. This extra momentum from the diffracted light gives us the needed momentum to create the surface plasmon.

This works well for plasmons in the visible light range but as the wavelength is decreased into the mid-IR and THz range the losses in metal increase significantly and the confinement goes down. For this case another material is needed. In chapter one we looked at graphene and some of it exotic properties. The plasmon resonance for graphene can be found by solving Maxwell’s equations and is

\[ q_{sp} = \frac{i2\omega \varepsilon_0 (\varepsilon_{r1} + \varepsilon_{r2})}{\sigma (q, \omega)} \]  

(39)

\[ \sigma (\omega) = \frac{iD}{\pi (\omega + i\tau^{-1})} \]  

(40)

\[ D = \frac{\nu_F e^2}{\hbar \sqrt{\pi n}} \]  

(41)

\[ q_{sp} = \frac{2\varepsilon_0 (\varepsilon_{r1} + \varepsilon_{r2}) h\pi}{\nu_F e^2 \sqrt{\pi n}} \omega^2 \left(1 + i \frac{i}{\omega \tau}\right) \]  

(42)

\[ \omega^2 = \frac{q\nu_F e^2 \sqrt{\pi n}}{2h\pi \varepsilon_0 (\varepsilon_{r1} + \varepsilon_{r2})} \frac{1}{1 + \frac{1}{\omega \tau}} \]  

(43)

\[ q = (2n + 1) \frac{\pi}{\omega} \]  

(44)

\[ \omega^2 = \sqrt{\pi} \frac{\nu_F e^2 \sqrt{\pi}}{W^2 2h\pi \varepsilon_0 (\varepsilon_{r1} + \varepsilon_{r2})} \frac{1}{1 + \frac{1}{\omega \tau}} \]  

(45)

In this case \( \sigma (\omega) \) is the conductivity of graphene where \( D \) is the Drude value using MDF’s. Graphene is much better at low frequencies than metals due to a lower
conduction loss. However as the frequency increases interband translations occur and contribute largely to the loss in graphene plasmonics above THz frequencies. From Eq. 45 we can see that $\omega_p \propto (n)^{1/4}$ and $\propto W^{-1/2}$ the charge density and width of the micro ribbon respectively. This allows us to tune the plasmon resonance frequency with the width of the ribbons and actively tune the frequency by doping or adjusting the charge density. Changing the charge density can be done by gating the graphene like in a transistor. By applying a voltage between the gate and the graphene the charge density can be tuned. Here we see that as the voltage increases the resistivity also increases due to the increase in doping.

Recently graphene nanoribbons (GNRs) have also evolved as a unique material entity due to some characteristics such as highly reactive GNR edges [97, 98], bandgap formed for narrow GNRs [99], highly inhomogeneous charge distribution within GNRs [100], and the self-doping effect [101, 102] which all scale with GNR width. Moreover, GNRs could exhibit different edge geometries including zigzag and armchair, which will determine their electronic structures [103]. Theoretical studies on GNRs doped with N, B, and O atoms have demonstrated that the edge-type, as well as the substitutional doping, could induce a half-metallic behavior and the band gap could be tuned by doping [104]. While doping of bulk-graphene has been performed for numerous purposes including modification of the electronic and quantum transport properties, doping of GNRs has been performed mostly for dynamic tuning of plasmon resonance absorption spectra of GNRs. The relatively new field of graphene plasmonics has attracted interest due to graphene’s unique tunability over a broad range, long plasmon lifetime, and high degree of electromagnetic confinement [105, 106]. Remarkably large oscillator strength of patterned graphene micro-ribbons in the THz frequency regime [107, 108] has resulted in room-temperature resonant absorption strengths as high as 13% [109]. This prompted studies in the mid-IR involving GNRs [110, 111, 112, 113, 114, 115]. Mid-IR studies highlighted graphene plasmon damp-
ing channels including graphene’s intrinsic optical phonon frequency at 0.2 eV which limits the quality factor of the plasmon resonance for higher frequencies [112]. The most visible substrate effect in mid-IR absorption spectra of GNRs are the unexpected resonances around 110 meV (900 cm\(^{-1}\)) which is understood as arising from strong coupling between the graphene plasmons and the surface optical (SO) polar phonons of the SiO\(_2\) substrate. These resonances are modeled as hybrid surface plasmon phonon polaritons (SPPPs) modes. Given the significantly long lifetimes of these SO phonons (\(\sim\)pSec). In electronics, substrate-dependent effects such as doping has been confirmed by electrical measurements for the graphene transistors made on various substrates [116, 117]. Also, it is well known that the surface roughness and charge impurities in the underlying SiO\(_2\) substrate, for example, lead to doping in the form of electron-hole charge fluctuations or puddles [118]. Some studies have shown that the effective doping from the underlying substrate is predominant rather than the effective gating from substrates [119]. It is also reported that the contact potential difference between SiO\(_2\) substrates and graphene controls the direction of the dipoles formed at the interface. The substrate-induced electron injection (depletion) in graphene actually imposes effective \(n\)-(\(p\)-) doping to the graphene. Also, any polar contaminant adsorbed on the top surface of graphene also influences the charge fluctuation and acts as dopants. In the case of GNRs, in addition to above mentioned doping effects, highly reactive edges and inhomogeneous charge distributions are known to attract functional electro-negative/positive molecular groups that is shown to shift the Fermi level. Electron beam exposure (EBE) of graphene or GNRs on SiO\(_2\) substrate can be an effective method for modifying their carrier density given the existence of SiO\(_2\) surface states that can hold quasi-charge densities as high as \(3.2 \times 10^{12}\) cm\(^{-2}\) over prolonged periods of time. A previous study has reported that low-energy, low-dose EBE of bulk-graphene causing n-type doping in addition to the modification of graphene-SiO\(_2\) substrate interaction [120].
These measurements made use of the stiffening of the Raman G-band with doping and the narrowing of the G-band FWHM. These results were important for validating conclusions from the e-beam irradiation experiments mentioned above regarding carrier doping. Raman spectroscopy has also been a useful tool in providing GNR microscopic information such as the amount of disorder, doping as well as the atomic arrangements at the edges. In this paper, we use infrared and Raman spectroscopy to demonstrate that upon direct e-beam exposure, the charge exchange with the substrate has resulted in n-type doping for GNRs and p-type doping for bulk graphene. In the presence of highly reactive GNR edges and SiO$_2$ surface states that can hold quasi-charge densities as high as $3.2 \times 10^{12}$ cm$^{-2}$ over prolonged periods of time, we show that carefully chosen low-doses of EBE of graphene or GNRs on SiO$_2$ substrate can be an alternative method to effectively change their carrier density. EBE-induced charging of SiO$_2$ substrate and any charge exchanges at the edges can lead to measurable doping of GNRs. This was observed in red-shifting of plasmon resonance absorption spectra for GNRs of various widths. We correlate the optical extinction spectra obtained by infrared spectroscopy with the Raman spectra for GNRs to show that EBE causes additional doping or counter-doping of graphene away from the charge neutrality. The purpose of these studies was to get an insight into the charge inhomogeneity within a given GNR on SiO$_2$ substrate resulting from edge effects and their contribution towards total change in carrier density upon ebeam exposure of GNRs. Our experimental results on graphene plasmon resonances were compared with finite-difference-time-domain (FDTD) simulations with graphene's complex optical conductivity evaluated within the local random phase approximation (RPA).

4.2 Experiments and Methodology

Several samples were fabricated for transmission spectrum testing using a Fourier transform interferometer (FTIR) with an attached microscope. Graphene micro-
Figure 44: Optical images of graphene micro-ribbons with a graphene width of 4μm and a spacing of 3μm (a), antidots with a diameter of 3μm and spacing of 1μm (b), and islands with an average diameter of 5.25μm (c).

Figure 45: Optical image of gated graphene micro-ribbons (a) and resistance vs gate voltage for micro-ribbon shown in figure 44a.

ribbons, graphene antidots, and graphene islands (Fig. 44). The graphene for the micro-ribbons and antidots was transferred and patterned as described in chapter 3. The graphene for the graphene islands was grown on a Cu substrate but so that the growth was not complete. This was then transferred to a Si/SiO$_2$ substrate using the above mentioned technique.

The micro-ribbons were patterned with a source and drain (Fig. 45) in order that the doping could be verified. This was done by applying a constant voltage across the source and drain (0.1V) and using the Si as the gate conductor and the bottom SiO$_2$ as the gate dielectric the gate voltage was varied from -10 to 30V.

We used graphene grown on 25 μm-thick copper foil using chemical vapor deposition (CVD) method. After being transferred to SiO$_2$/Si wafers, GNR arrays were patterned using an ebeam lithography system with a 100kV energy beam. Graphene
Figure 46: Plasmonic resonant absorption experiment with GNRs and introduction to its tunable, polarization-sensitive spectra. (a) Schematic of the sample. (b) FDTD simulation of $|E(x, y)|^2$ on the surface of a GNR of width $W=125$ nm ($\mu=1000$ and $E_F=0.4$ eV) (c) FDTD simulation of tuning of transmission spectra for an array of GNRs for varied Fermi levels. (d) The extinction spectra of an array of GNRs ($W=125$ nm) on SiO$_2$ with the incident light polarization parallel (red) and perpendicular (black) to the ribbons respectively (weak 2nd order mode can be seen); inset shows a SEM image of 135 nm wide GNR array.

was then etched using oxygen plasma reactive ion etching. Using this process we were able to fabricate GNRs over 200 by 200 $\mu$m$^2$ areas with their widths varying from 215 nm to 55 nm. The substrate for all of the samples was 290 nm thick SiO$_2$ on top of phosphorus doped n-type silicon wafers with resistivity in the range of 1 to 30 Ohm-cm. Hall measurement of transferred graphene samples in the same batch as GNRs confirmed a p-type carrier density in the range of $1$ to $3 \times 10^{13}$ cm$^{-2}$ and mobility value around $1000$ cm$^2$V$^{-1}$Sec$^{-1}$.

To measure the transmission spectra of the graphene resonator arrays, we used a Fourier transform interferometer (FTIR) with an attached microscope. The infrared
was polarized by a CaF₂ wire grid polarizer. The measurement focused spot size on
the GNRs was approximately 50μm x 50μm, significantly smaller than the area of
the arrays (200μm x 200μm). IR transmission spectra from 700 to 3000 cm⁻¹ were
collected for GNRs with widths of W~ 55, 75, 95, 135, 165, 215 nm as determined by
SEM. A figure of merit for absorption was calculated from the transmission spectrum
defined as 1−T⊥/T∥ where T⊥ and T∥ are transmittance with polarization perpendicu-
lar and parallel to the GNR ribbons respectively. T⊥ and T∥ each were measured with
a reference transmission measurement completed on SiO₂ for each respective polarization. The transmission spectra of an array of GNRs on a SiO₂ substrate, pictured
in Figure 46b, were simulated with finite-difference time-domain method (FDTD) in
Lumerical solutions™. In the simulations, the graphene was modeled as a thin layer
with a thickness 0.5 nm and an anisotropic dielectric constant described by a diagno-
tial tensor. The in-plane dielectric tensor component is \( \varepsilon_{r11} = \varepsilon_{r22} = 2.5 + i\sigma/(\varepsilon_0\omega t) \),
where \( \sigma \) is the frequency-dependent conductivity of doped graphene in the Drude
model, and the surface-normal component is set as \( \varepsilon_{r33} = 2.5 \) based on the dielec-
tric constant of graphite. For the SiO₂ substrate, frequency-dependent SiO₂ material
data contained in Lumerical solutions™ was used. In the electron beam exposure
experiments, bulk graphene as well as GNRs were ebeam exposed by using the Tes-
can LYRA-3 (Model XMH I) SEM system which allowed for accurate control of the
exposed area and dose. For all experiments, we used an ebeam accelerating voltage
of 15 keV, a working distance of 6 mm, a beam current of 300 pA measured with a
Faraday cup, and an exposed area of 200μm x 200μm.

4.3 Results and Discussion

The resonance spectrum for the graphene micro-ribbons are presented in Fig. 47,
antidots Fig. 48 and graphene islands Fig. 49

In figure 47a there is a clear plasmon resonance for both the 45 and 90 degree
polarization where as for the parallel degree polarization no resonance shows up. This is as expected since the plasmon excitation is heavily localized across the ribbons and depends strongly on the width of the ribbon. Furthermore the absorption for the perpendicular polarized light is stronger than that of the 45 degree polarized light. This is due to only a portion of the incident light being able to couple with the plasmon modes. In figure 47b a numerical simulation was ran using Lumerical’s FDTD software. In this simulation a single 5μm graphene ribbon suspended in air had perpendicular polarized light incident onto it and the transmission spectrum was acquired. A clear absorption peak can be seen at 200 cm$^{-1}$ along with resonance peaks at higher wavenumbers. This is close to the 150 cm$^{-1}$ absorption peak that we see from the experimental values.

In figure 48 we see the spectrum for graphene antidots. The absorption peak is located at 70 cm$^{-1}$. In this case the resonance is not dependent on polarization due to the 2D nature of the pattern.

Figure 49 shows the transmission spectrum for graphene islands at two separate locations. For location 1 there were very few graphene islands so the absorption was very week and can barely be seen. In location 2 the graphene islands were very dense and showed an absorption of around 15%. These experiments verify the analytical models that were developed in section 1.
Figure 48: Graphene antidot spectrum taken using FTIR for no polarization (a), 0 deg polarization (b), 45 deg polarization (c), and 90 deg polarization.

Figure 49: Graphene Islands spectrum
Figure 46 shows infrared spectroscopy experiment on GNRs and the resulting plasmonic resonant absorption spectra. Figure 46(a) shows a schematic of GNRs on SiO$_2$ substrate while Figure 46(b) shows $|F(x, y)|^2$ on the surface of a GNR for the fundamental mode following a FDTD simulation where we used the values: GNR width $W=125$ nm, the graphene mobility $\mu=1000$ cm$^2$/Vs, and Fermi level $E_F=0.4$ eV. This is in agreement with previously reported work [105] where high electric field confinement at GNR edges and the resonances were understood using a simple Fabry–Perot model of localized plasmons bound in GNRs. Figure 46(c) shows further FDTD simulation-generated results depicting the tunability of the plasmonic resonant absorption spectra. Distinct polarization-dependence is visible in figure 46(d) where the spectra corresponding to perpendicular (parallel) polarization with respect to the length of GNRs are shown in black (red). Three major resonance peaks are identified within our measured frequency range of 700 to 3000 cm$^{-1}$. As theoretically predicted, only the perpendicularly polarized light exhibits the peaks around 900 and 1300 cm$^{-1}$ (0.125 and 0.185eV), which are associated with the plasmon resonances. It should be noted that the multiple resonance peaks observed here are in sharp contrast to the far-IR spectra of graphene microstructures, which usually display a single strong resonance. Without plasmon excitations, the spectrum with parallel polarization does not show resonance peaks except for small features from 900 cm$^{-1}$ to 1200 cm$^{-1}$. These features are related to the fast-varying dynamic dielectric function of the SiO$_2$ substrate, and are quite weak (< 1% in extinction) compared to the high contrast plasmon peaks. In these mid-IR wavelengths, if the light is polarized parallel to the highly doped graphene ribbons, their interaction is insignificant due to the Pauli blocking of interband transitions and the weakness of the free-carrier intraband transitions in such high frequencies. Inset in figure 46(d) shows a SEM image of nanofabricated GNR array of period $p=180$ nm and width $W=135$ nm.

Figure 50(a) and (b) respectively show experimental and FDTD simulation results
Figure 50: Experimental extinction spectra of GNRs on a SiO$_2$ substrate (a) Experimental extinction spectra ($1 - T_{\text{per}}/T_{\text{par}}$) of graphene nanoresonators for varying GNR widths; spectra are offset for clarity. The spectra were referenced using transmission of light with parallel polarization ($T_{\text{par}}$) (b) the same obtained by FDTD simulations ($\mu=1000$ and $E_F=0.265\text{eV}$).

for the extinction spectra for GNRs on SiO$_2$ substrate with their width $W$ ranging from 55 to 215 nm (with 50% duty cycle). The multiple resonance absorption peaks observed in all spectra are due to the interactions of graphene plasmons with substrate phonons. All resonance peaks blue-shift as $W$ decreases but at significantly different rates. In particular, the peak marked 3 disperses at a much faster rate with frequency. We also observe the transfer of spectral weight from peak 1 to peak 2 and 3 as $W$ decreases, and eventually peak 3 retaining most of the spectral weight for $W < 75$ nm. The resonance linewidth for peak 3 increases with decreasing $W$, while those of peaks 1 and 2 remain almost constant. The linewidth is directly related to the plasmon damping and, for peak 3, strongly depend on $W$. It is also important to note that peak 3 is very asymmetric, especially for relatively narrow GNRs; the line shape is well described by the Fano resonance model in Ref [111]. By tuning GNR width, we have been able to probe graphene plasmons with plasmon resonances as high as $.240\text{eV}$ ($\sim2050\text{ cm}^{-1}$) for 55 nm wide GNRs. The graphs in figure 50(a) also show that the damping of hybrid plasmon-phonon modes, specifically, damping for peaks 1 and 2 is determined by the surface optical phonon lifetime which is typically a few picoseconds. The modes described by peak 1 and 2 are therefore more phonon-like for
large W since they resonate near SiO\textsubscript{2} SO phonon frequencies $\omega_{sp} \sim 58.9$ and 156.4 meV. This explains the lower damping rate of this mode in the large W limit. On the other hand, the mode described by peak 3 disperses rapidly in frequency and becomes more plasmon-like, especially for narrower ribbons. When the plasmon frequency is larger than graphene’s intrinsic phonon frequency of 1580 cm$^{-1}$ ($\sim$0.2 eV), the plasmons decay into electron-hole pair via the emission of a graphene optical phonon, which explains the larger damping for narrower GNRs. These observations agree well with previously reported work on graphene plasmonics in mid-IR. In the next section, we examine the modification of above discussed hybrid plasmon-phonon modes upon EBE of the same set of arrays of GNRs used for results in figure 50. Previously, numerous electron beam induced effects that occur at the interface between graphene and SiO\textsubscript{2} are reported. It will be interesting to study how such effects affect the plasmonic response of GNRs. It is known to be affected strongly by interactions with substrate surface optical (SO) phonons and the graphene intrinsic phonons. Since radiative damping in graphene nanostructures is expected to be negligible and due to the fact that plasmon excitations in our devices lie outside of the Landau damping regime, the plasmons are expected to decay primarily by inelastic scattering with phonons [123, 124] and elastic carrier scattering processes [125]; thus, contributing to the plasmon damping. These two processes can be important for large plasmon energies (i.e. $\hbar\omega_{pl} > 0.2$ eV) and small dimensions respectively. Interactions with the SO phonons can also influence the lifetimes of the hybrid plasmon-phonon modes, especially when the energy of the hybrid mode is close to that of the SO phonons. When graphene is placed on a polar substrate accommodating these SO phonons, the long-range Fröhlich coupling can mediate interactions with the electronic degrees of freedom in graphene, including the collective plasmon modes. These interactions lead to the renormalization of the plasmon dispersion as well as to govern the lifetimes of plasmons. It is important to note that FDTD simulated results, shown in figure
Figure 51: Raman spectra of GNRs in comparison with unpatterned graphene. (a) Raman spectra for GNRs of various widths and bulk graphene for 532.3 nm wavelength laser excitation (b) Plot of I(2D)/I(G) and I(D)/I(G) for GNRs of various widths and for bulk graphene.

50(b), also show the above described characteristics for the extinction spectra except the damping observed due to graphene’s intrinsic optical phonons. Here we show the doping level for bulk as well as GNRs using Raman spectroscopy.

Figure 51(a) shows the Raman spectra of GNRs alongside of bulk graphene for excitation with laser wavelength $\lambda = 532$ nm. As reported elsewhere [126, 127], two defect-induced bands at $\sim 1330$ cm$^{-1}$ (D band) and at $\sim 1620$ cm$^{-1}$ (D* band) dominate the spectra as the GNR width decreases. The increasing D-band intensity is due to the increasing fraction of edge carbons where the edges serve as defects due to breaking of the translational symmetry of the lattice [116, 128, 129]. We also observe a slight upshift in the G-band and a drastic broadening in the G bands for narrower GNRs, which can be attributed to the size- and edge-effects. It is also observed that as one moves from bulk graphene to narrower GNRs, the spectral weight shifts from 2D-band to G-band to D-band. In figure 51(b) where we have summarized the spectra, I(D)/I(G) increases significantly for narrower GNRs. On the other hand, I(2D)/I(G), a sensitive indicator for doping level in graphene as previously reported [130, 131], decreases with increasing GNR width. As ribbon width decreases, edges represent
a larger fraction of total carbons and thus become more important. In particular, our ribbons were patterned using oxygen plasma, a harsh oxidizing condition, which is known to form various oxygen-containing functional groups on graphite. Since oxygen is more electronegative than carbon, such functional groups are expected to withdraw \( \pi \) electrons of GNRs (i.e., dope with holes). Thus, to be consistent with previous reports [100, 117, 127, 132] and our Hall measurements performed on bulk graphene, our GNR arrays are doped more heavily in p-type. Similar dependence of \( I(2D)/I(G) \) on GNR width have been reported elsewhere. Figure 51(b) also show that for \( W > 100 \) nm, \( I(2D)/I(G) \) value is roughly equal to that of bulk graphene. The observed dependence of \( I(2D)/I(G) \) on GNR width can be explained in terms of the self-doping effect in GNRs which shifts GNR doping level from that of the original bulk graphene that was used to create GNRs.

In this section we discuss tuning of SPPP spectra by ebeam exposure. Here we show low-energy ebeam irradiation of GNRs on SiO\(_2\) substrate in effect induces counter-doping of originally p-doped GNRs. Based on the fact that surface states of SiO\(_2\) can accommodate charged densities as high as \( \sim 3 \times 10^{12} \) cm\(^{-2}\) over prolonged periods of time, through multiple steps of EBE, we gradually increased the accumulation of charge on SiO\(_2\) which in effect created the necessary charge traps or impurities to change the carrier density in GNRs and in bulk graphene. We observed the resulting decrease in carrier concentration in GNRs in red-shifting of SPPP spectra.

Figure 52 shows the SPPP spectra for 3 different GNR widths (95, 125, and 215 nm) for increasing EBE dose levels. As expected, the shifting of SPPP spectra for all 3 GNRs reached saturation for an accumulated ebeam dose value \( \sim 20 \times (2.25 \times 10^{-1} \mu \text{C/cm}^2) \). For resonator width \( W=95 \) nm, EBE caused the SPPP spectra red-shifted closer to the vicinity of surface polar phonons at 1168 cm\(^{-1}\) and 806 cm\(^{-1}\) for SiO\(_2\) which feature a long lifetime. The shifting of low energy, phonon-like peaks (peak 1 & 2) are much less dependent on the EBE dose. Interestingly, narrower GNR respond
Figure 52: Tuning of SPPP spectra by ebeam exposure (EBE) for 3 different GNRs of width $W=95$, 125, and 215 nm upon increasing doses of EBE.
stronger than wider GNRs in response to EBE. These observations are similar to previously reported, gate-induced tuning of graphene SPPP spectra in mid-IR [105, 112].

EBE-induced filling of surface states of SiO$_2$ substrate and the resulting charge density change on SiO$_2$ is likely to induce charged impurities trapped at the graphene-substrate interface for causing additional doping or counter-doping of GNRs away from the charge neutrality. These charge impurities are shown to introduce point defects, like impurities and vacancies on graphene. Such defects can nucleate a few electronic states in their vicinity. Hence, a concentration of $n_i$ impurities per Carbon atom leads to a change in the electronic density of the regions between the impurities of order $n_i$. Assuming a homogeneously induced distribution of impurities in GNRs upon EBE and using the relationship $\omega_p \propto n_i^{1/4}$, the corresponding change carrier density in GNRs $\Delta n_i$ was calculated to be $1.72 \times 10^{13}\text{cm}^2$ (using the spectral shift in GNR with $W=95$ nm).

4.4 Conclusions

By using infrared and Raman microscopy and direct ebeam exposure, we highlighted edge effects such as self-doping effect in GNRs. Direct ebeam exposure of GNRs on SiO$_2$ substrate was shown in effect to electron-doped GNRs which was evident in red-shifting of their plasmon resonant spectra. This study also provided the experimental evidence for relative contribution of edge doping in overall carrier density in graphene nanoribbons which enabled us to verify fundamentally different ways of charging/de-charging for bulk graphene and graphene nanoribbons. By mapping of plasmon dispersion curves, we showed the need for scaling of the Fermi energy of graphene nanoribbons with their widths. Results from our Raman study showed that the G and 2D peaks have different doping dependence and their intensity ratio was effective in responding to charge neutralization or exchange between charged impurities on SiO$_2$ with ebeam induced charge carriers on graphene surface/edges. This in
effect revealed the importance of including finite-size effects such as the divergence of the carrier density at graphene ribbon edges for narrower graphene ribbons in understanding the optical response of GNRs. The results postulate the possibility of tuning electronic property of graphene devices by substrates. These results have important implications to further our understanding of basic electronic properties such as carrier screening, scattering, and energy dissipation. Most importantly, our study provides basic guidelines for future nano-scale plasmonic graphene devices.

5 Magnetic Materials

Metallic ferromagnetic (FM) thin films provide a unique opportunity for integrated radiofrequency (RF)/microwave magnetic devices such as antennas, filters, inductors, etc. in the GHz range [44, 45, 46]. Despite continuous efforts to develop FM materials over the past three decades [47, 48, 49], developing integrated circuit (IC)-compatible magnetic materials with high permeability, high ferromagnetic resonance frequency (FMR), and low losses still represents a formidable challenge. Governed by the Landau-Lifshitz equation [50], the magnetic permeability is mainly determined by the saturation magnetization, ferromagnetic resonant frequency, magnetic anisotropic field, damping factor, external magnetic field, and shape-induced demagnetizing factor. Apart from these, the conductivity of the magnetic material and the induced eddy current at radio frequency (RF)/microwave frequencies deteriorate the magnetic permeability and significantly increase the loss. In fact, the high conductivity imposes a formidable challenge in applying metallic ferromagnetic thin films in integrated RF/microwave circuits, though many efforts have been made to develop high resistivity magnetic nano-granular films. Bulk microwave ferrite materials were widely used in early RF/microwave devices. However, the high processing temperature, Snoek’s frequency limit, and the need for external biasing magnetic fields impede
their integration into standard complementary metal-oxide-semiconductor (CMOS) technology. Recently, low-temperature spin-sprayed ferrite films (Fe$_3$O$_4$) with a high self-biased magnetic anisotropy field have been reported showing FMR frequency $>5$ GHz [51]. Such films hold great potential for RF/microwave devices and find immediate applications in patch antennas and bandpass filters [52, 53, 54, 55, 56]. These films also hold great potential for radio frequency (RF)/microwave devices for the superior electrical and magnetic properties [57, 58, 59, 60, 61]. The low processing temperature and the wide substrate compatibility make the deposition method compatible with the standard silicon technology, enabling to make integrated planar microwave devices [62, 63]. Recently, a few groups reported spin-sprayed deposition of Fe$_3$O$_4$. The Fe$_3$O$_4$ shows to be more environmentally friendly than others, like NiZn which consists of heavy metal. The real part magnetic permeability above 20 has been obtained at 0.2 GHz [64]. Among all the challenges, suppression of loss at RF/microwave frequency of spin-sprayed Fe$_3$O$_4$ is of key importance, which relies on the understanding of the loss mechanisms. The temperature-dependent electrical resistivity of Fe$_3$O$_4$ has been reported by a few groups, indicating higher resistivity at the grain boundary than in Fe$_3$O$_4$ grains [65, 66]. This conclusion was drawn by performing resistivity measurements over a large area crossing multiple grain boundaries. In the model, the grain boundary forms a potential barrier to prevent tunneling current between the grains. To date, few published works have addressed in situ characterization of the electrical resistivity of a single grain boundary [67, 68, 69], and the measurements were carried out either at zero or low frequencies. In this study, we performed in situ scanning microwave microscopy (SMM) characterization of a thin Fe$_3$O$_4$/photoresist (PR)/Fe$_3$O$_4$ film at frequencies between 2.0 GHz and 8.0 GHz. By comparing these results with a reference sample of known conductivity, it was clearly visualized that the grain boundary had higher electrical conductivity than the grains. Three single layered Fe$_3$O$_4$ samples were investigated with various thicknesses, grain
sizes, and electrical conductivities [70]. The SMM has the ability to measure both the
topography and the electromagnetic wave reflectivity at RF/microwave frequencies
of a sample. The results show that the grain boundaries are more conductive than
the grains themselves in the Fe$_3$O$_4$ samples.

5.1 Experiments

For this there were four samples fabricated for measurements. The first ferrite spec-
imen consisted of three layers: Fe$_3$O$_4$ (1.2 µm)/PR (60 nm)/Fe$_3$O$_4$ (1.2 µm). The
Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer thin film was fabricated at 90°C by spin-spray deposition
onto commercially available, 0.1-mm-thick glass substrate. An oxidation solution con-
taining 2 mM NaNO$_2$ and 140 mM CH$_3$COONa with pH value of 9 and a precursor
solution containing 10 mM Fe$^{2+}$ with pH of 4 were sprayed simultaneously through
two separate nozzles onto a glass substrate rotating at 145 rpm in the presence of N$_2$
gas. The growth rate was 40 nm/min. After an approximate thickness of 1.2 µm, a
thin layer of PR was deposited by spin coating at 2500 rpm for 0.5 min, and then
annealed at 100°C for 10 min to form a 60-nm nonmagnetic layer. Another layer of
Fe$_3$O$_4$ was then deposited with total thickness of 2.4 µm. The PR layer served as
an insulation layer to prevent current flow between the two ferrite layers. The mag-
netic properties of the film were measured using a vibrating sample magnetometer
(VSM) with an external magnetic field applied parallel (in-plane) and perpendicular
(out of plane) to the film plane. The film exhibited in-plane coercivity of 118 Oe,
saturation magnetization of 398 emu/cm$^3$, and electrical resistivity of 7 Ω cm. Mag-
netic permeability spectra were measured on a broadband custom-made Permeameter
(0.045 GHz to 10 GHz) consisting of a coplanar waveguide. The film demonstrated
a FMR frequency of 1.2 GHz. The FMR linewidth was measured to be around 464
Oe at X-band (9.6 GHz) by electron paramagnetic resonance (EPR). In situ electric-
cal characterization was performed on an Agilent 5420, which consists of an atomic
force microscope (AFM) and a microwave network analyzer (PNA). The PNA records one-port scattering parameters \(s_{11}\) in a broad frequency range from 2.0 GHz to 8.0 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 (30 nm) due to the enhanced electromagnetic field at the tip end. For comparison, a reference sample with a 5 nm thick partially oxidized graphene nanosheet on a platinum surface was measured. Three \(\text{Fe}_3\text{O}_4\) films were prepared by spin-spray method. A reaction solution containing 20mM \(\text{FeCl}_2\cdot4\text{H}_2\text{O}\), and an oxidizing solution containing oxidizing agent of 65mM \(\text{CH}_3\text{COOK}\) and pH regulator of 5mM \(\text{KNO}_2\) were sprayed simultaneously onto the substrates heated at 95°C. Three \(\text{Fe}_3\text{O}_4\) samples with different length of growth times were investigated and their growth parameters are listed in Table 5. The electrical conductivity increases as the film thickness increases, indicating a higher conductive loss in thicker film. The SMM measurements were taken using an Agilent 5420 AFM connected to an Agilent PNA (performance network analyzer) N5230C. In this way, the SMM tip acts as a waveguide and can measure the reflection coefficient \(s_{11}\). The SMM was operated in constant force contact mode during all of the measurements. The SMM was lowered into contact with the sample and then raised 20 µm from the sample. This created an open waveguide. A frequency sweep was performed from 1.5 GHz to 18 GHz in order to find both the half wavelength and quarter wavelength frequencies. The frequencies obtained were 17.13 GHz for the half wavelength case and 16.53 GHz for the quarter wavelength case. The half wavelength frequency was set, and the tip was lowered into contact with the sample then raster scanned across the sample. This was repeated for the quarter wavelength case on all three samples.
Figure 53: Comparison of SMM images acquired from the same region at two different frequencies: (b) 2.5867 GHz and (c) 2.2282 GHz. The image on the left (a) shows the surface topography by AFM.

Using this method, the topography, $s_{11}$ amplitude, and $s_{11}$ phase were obtained simultaneously. The iron oxide samples were inserted into a transmission line based permeameter. The transmission line consists of a pair of parallel copper strips 1 mm wide and 3 cm long for each strip. The distance between the two strips was 1 mm. Magnetic permeability and insertion loss were measured by performing single port S-parameter measurement on Agilent E5061B, while the other port was short-circuited or open-circuited. The measurements of the permeability and the insertion loss measurements were performed between 10 and 300 MHz, above which the LC resonance starts to play a dominant role.

5.2 Results and Discussion

The SMM system renders simultaneously acquired information of the amplitude and phase of $s_{11}$, and the surface topography. Figure 53a shows a surface morphological image of the ferrite multilayer, showing pebble-stone-shaped particles with size ranging from a few hundred nanometers to a couple of microns. Prior to each SMM imaging, a frequency scan between 2.0 GHz and 8.0 GHz was performed to identify resonant peaks. Usually, multiple resonant peaks could be registered in this frequency range. To correlate the SMM images and the electromagnetic properties of the sam-
ple, SMM images were recorded at every resonant peak. It was observed that both
the amplitude and the phase angle of $s_{11}$ depended on the measurement frequency,
the shape and the order of the resonant peak, and the offset frequency with respect to
the resonant peak. Figure 53b and c show two examples of the recorded amplitude,
at 2.5867 GHz and 2.2282 GHz, respectively. Comparing Fig. 53b with Fig. c, the
contrast of the grain boundary and the grain is reversed: The grain boundary was
bright in contrast to the grains in Fig. 53b, while it becomes dark relative to the
grains in Fig. 53c. It is noteworthy that the two measurements were performed at
the same location. 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 perme-
ability spectra measurement, above the ferromagnetic resonant frequency $\sim 1.2$ 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 com-
plex dielectric constant $\varepsilon$ in general depends on the operating frequency ($\omega$, angular
frequency), the real part of the dielectric constant ($\varepsilon'$), and the conductivity of the
sample ($\sigma$):

$$\varepsilon = \varepsilon' + \frac{\sigma}{j\omega} \quad \quad (46)$$

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 the electric
properties of the sample, an equivalent circuit model was established as shown in
Fig 54. The model consists of a transmission line with length $l_0$ and characteristic
impedance $Z_0 = 50 \Omega$. The length of the transmission line was designed to approx-
imately equal a 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
The 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 \( 1/\omega C \gg Z_0 \)) 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 is shunted with a 50 \( \Omega \) resistor. As for a one-port system, according to the transmission line theory, \( s_{11} \) is equal to the reflection coefficient \( \Gamma \) and can be written as

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

(47)

where

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

(48)

Here \( \omega \) is the angular frequency, and \( \beta \) is the wavenumber. To derive the correlations between \( \Gamma \), \( R \), and \( C \), Eq. 47 needs to be further simplified. When the frequency approaches the \( \lambda/2 \) resonant frequency, the amplitude \( |\Gamma| \) and phase angle \( \theta \) of \( \Gamma \) in Eq. 47 become

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

(49)

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

(50)
In practice, the $\lambda/2$ resonance was recognized by choosing the peak with phase angle $\theta \approx -\pi/2$, because when the SMM tip was lifted up in the air, $R$ approached infinity leading to phase angle close to $\theta \approx -\pi/2$. 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 $\theta$; high dielectric constant will increase $|\Gamma|$ and $\theta$ simultaneously. SMM images of $|\Gamma|$ and $\theta$ recorded at $\theta = -93.4^\circ$ and $f = 2.4868$ GHz are shown in Fig. 55a and b. The grain boundary had a larger value of $|\Gamma|$ (Fig. 55a) and smaller value of $\theta$ (Fig. 55b), thus verifying a higher electrical conductivity at the grain boundary than in the grain. The above argument is supported by performing SMM measurements at $\lambda/4$ resonance. When the frequency approaches the $\lambda/4$ resonant frequency, the amplitude $|\langle \Gamma \rangle|$ and phase angle $\theta$ of $\Gamma$ can be simplified from Eq. 47 to be

$$|\Gamma| \approx 1 - 2Z_0 \sqrt{\frac{1}{R^2 + \omega^2 C^2}}$$

(51)

$$\theta = - \tan^{-1} \left( 2Z_0 \sqrt{\frac{1}{R^2 + \omega^2 C^2}} \right)$$

(52)

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 $\theta \approx 0$. SMM images of $|\Gamma|$ and $\theta$ recorded at $\theta = 2.81$...
Figure 56: SMM images of the amplitude $|\Gamma|$ (a) and phase angle $\theta$ (b) of the reflection coefficient recorded at $\theta = 2.81$ and $f = 6.2688$ GHz. Since the length of the transmission line is designed to be $\lambda/2$ at 2.5 GHz, $f = 6.2688$ GHz coincides with the second-harmonic $\lambda/4$ resonance above 2.5 GHz.

and $f = 6.2688$ GHz are shown in Fig. 56a and b. The grain boundary had smaller values of $|\Gamma|$ (Fig. 56a) and $\theta$ (Fig. 56b), which coincides with the measurements in Fig. 55. 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 Fig. 57. 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 Fig. 57b, 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 Fig. 57a 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. [133], who discovered a conductive path for electrons along the grain boundary, which proves to be beneficial for the performance of polycrystalline solar cells. According to the grain boundary space-charge model, the mixed ionic and electronic boundary contains a grain boundary core and two adjacent space-charge regions. Accumulation of charges in the space-
Figure 57: SMM images of the ferrite film (a) and the graphene oxide reference (b) at 2.3909 GHz. Note that the graphene nanosheets in this study are partially oxidized with poor conductivity, while the platinum substrate is highly conductive.

charge region has been revealed by a number of groups. The accumulated charges, we believe, play an important role in the enhancement of the local grain-boundary conductivity, leading to the contrast in the SMM image. It is worth mentioning that such enhancement only occurs along the grain boundary. Perpendicular to the grain boundary, the two adjacent space-charge regions can be considered as double Schottky barrier, blocking current flow from grain to grain, and imposing high resistance across the grain boundary.

The complex magnetic permeability of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer was measured and shown in Fig. 58. Simulations were performed based on the parameters listed in Table 4. The Landau-Lifshitz phenomenological damping constant $\alpha$ was assumed to be $\sim$0.46 in the simulation in order to obtain a reasonable fit. The value is, however, far above the value of $\sim$0.011 obtained from the EPR in Table 4. This is partly because the broad band complex permeability measurement was done in the absence of external magnetic field, whereas the EPR measurement was performed.
Figure 58: Measured and simulated complex permeability spectra of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer. The Landau-Lifshitz damping constant $\alpha$ was assumed to be 0.46, and the other parameters used in the simulation are listed in Table 4.

Table 4: Summary of film structural and magnetic properties (saturation magnetization $M_s$, coercivity $H_c$, real permeability at 300 MHz $\mu_r^r$, and FMR linewidth $\Delta H$ at X-band (9.6 GHz)) of the ferrite/non-magnetic multilayers.

<table>
<thead>
<tr>
<th>Film structure</th>
<th>Thickness ($\mu$m)</th>
<th>$M_s$ (emu/cm$^3$)</th>
<th>$H_c$ (Oe)</th>
<th>$\mu_r^r$ (Oe)</th>
<th>$\Delta H$ (Oe)</th>
<th>$\rho$ (\Omega cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/PR/Fe$_3$O$_4$</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>
Figure 59: (a) Surface morphology of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer, (b) amplitude of the reflection coefficient of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer by SMM recorded at 2.3909 GHz, (c) surface morphology of the graphene oxide/Pt sample, and (d) amplitude of the reflection coefficient of the graphene oxide/Pt sample by SMM recorded at 2.3909 GHz.

in a strong external magnetic field. VSM measurements showed that there was no preferred in-plane magnetization direction. It should be pointed out that various microscopic origins might cause the increase of the damping factor, such as eddy current. The surface morphology of the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer in Fig. 59a showed pebble-stone shaped particles with sizes ranging from a few hundred nanometers to a couple of microns. The magnitude of the complex reflection coefficients was recorded by SMM and is shown in Fig. 59b. 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 Fig. 59a, there is a clear contrast between the inner grains and the boundaries in Fig. 59b. 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
Fig. 59b thus reflects solely the response of RF/microwave signals due to the different electrical properties of the materials. Measurements on a reference sample with known conductivity/resistivity were performed at the same frequency (Figs. 59c and d). The sample contained a 5 nm thick partially oxidized graphene nanosheet on a platinum surface. It is known that oxidized graphene has poorer conductivity than platinum. In Fig. 59d, the platinum substrate appears to be brighter than the graphene oxide, suggesting that the grain boundaries are more conductive than the grains in Fig. 59b. An equivalent circuit of SMM is shown in Fig. 54. The shunt capacitive component represents the dielectric property, and the resistive component represents the conductivity of the sample. The length of the transmission line was designed to be $\lambda/2$ at $\sim 2.5$ GHz, where $\lambda$ is the wavelength. Based on the transmission line theory, the amplitude $|\Gamma|$ and phase angle $\theta$ of the complex reflection coefficient can be written as Eqs. 53 and 54

$$|\Gamma| \approx \frac{Z_0}{2} \sqrt{\frac{1}{R^2 + \omega^2 C^2}}$$

$$\theta \approx \tan^{-1}(\omega RC)$$

where $\omega$ is the angular frequency. From Eqs. 53 and 54, the sample with the higher electrical conductivity, i.e., the lower value of R, will have a larger value of $|\Gamma|$ and a smaller $\theta$; the sample with higher dielectric constant will have larger values of both $|\Gamma|$ and $\theta$. Figure 55a and b show the measurements recorded at $\vartheta = -93.4$ and $f = 2.4868$ GHz. The grain boundary had a larger value of $|\Gamma|$ and a smaller value of $\theta$, thus verifying a higher electrical conductivity of the grain boundary than of the grain. In practice, the $\lambda/2$ resonance was recognized by choosing the peak with a phase angle $\theta = -\pi/2$. According to the grain-boundary space charge model, the mixed ionic and electronic boundary contains a grain boundary core and two adjacent space charge regions. The accumulation of charges in the space charge region has been revealed.
Figure 60: Surface topography of spin spray Fe$_3$O$_4$ for (a) #A with particle size of 0.063 μm$^2$, (b) #B particle size of 0.082 μm$^2$, and (c) #C particle size of 0.116 μm$^2$.

Figure 61: Measured the real part of magnetic permeability of #A, #B, and #C.

by a number of groups. The accumulated charges, we believe, play an important role in the enhancement of the local grain boundary conductivity, leading to the contrast in the SMM image. The excessive conductivity of the grain boundaries leads to significant eddy current and consequently increases the Landau-Lifshitz damping constant $\alpha$.

The topography of the Fe$_3$O$_4$ samples show grains varying in size from a few hundred nanometers to a few micrometers (Fig. 60). From a particle analysis, it can be shown that #A has an average particle size of 0.063 μm$^2$, #B has an average particle size of 0.082 μm$^2$, and #C has an average particle size of 0.116 μm$^2$. The measured real parts of the magnetic permeability of samples #A, #B, and #C (Fig. 61) show almost constant between 10 MHz and 300 MHz. SMM measurement results
of the \( s_{11} \) parameter recorded at half- and quarter-wavelength resonant frequencies on \#C are shown in Figs. 62 and 63, respectively. In Fig. 62, the grains’ boundaries are light, while the grains themselves are dark for the amplitude measurements and the grains’ boundary are dark, while the grains are light for the phase measurements. In Fig. 63, both the amplitude and phase of \( s_{11} \) of the grain boundaries are dark, while the grains are light. Similar correlation between the amplitude and the phase of \( s_{11} \) parameters has been observed in \#A and \#B. According to the transmission line model [50, 96] the amplitude \(|\Gamma|\) and phase \(\theta\) of \( s_{11} \) at half-wavelength resonance can be written to \(|\Gamma| \approx 1 - 2Z_0\sqrt{\frac{1}{R^2 + \omega^2C^2}}, \theta \approx \tan^{-1}(\omega RC)\), and the amplitude and phase of \( s_{11} \) at quarter-wavelength resonance are \(|\Gamma| \approx 1 - 2Z_0\sqrt{\frac{1}{R^2 + \omega^2C^2}}, \theta = -\tan^{-1}\left(2Z_0\sqrt{\frac{1}{R^2 + \omega^2C^2}}\right)\), where \( Z_0 \) is the characteristic impedance, \( R \) represents the resistivity of the sample, \( C \) represents the dielectric constant of the sample, and \( \omega \) is the angular frequency. Clearly, increase of sample’s conductivity (i.e., reduce \( R \)) leads to a greater \(|\Gamma|\) and a smaller \(\theta\) at half-wavelength resonance, and a reduced
Figure 64: Measured insertion loss of #A, #B, and #C per unit length. The insertion losses have been normalized to the Fe$_3$O$_4$ film thickness.

Table 5: Growth parameters of the three Fe$_3$O$_4$ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time (min)</th>
<th>Film thickness ($\mu$m)</th>
<th>Conductivity ($\Omega^{-1}$/cm)</th>
<th>Particle size ($\mu$m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#A</td>
<td>50</td>
<td>2.15</td>
<td>0.42</td>
<td>0.063</td>
</tr>
<tr>
<td>#B</td>
<td>60</td>
<td>3.30</td>
<td>0.77</td>
<td>0.082</td>
</tr>
<tr>
<td>#C</td>
<td>90</td>
<td>3.78</td>
<td>1.67</td>
<td>0.116</td>
</tr>
</tbody>
</table>

amount of $|\Gamma|$ and $\theta$ at quarter-wavelength resonance. Compared with the SMM measurements shown in Figs. 62 and 63, it turns out that the grain boundaries are more conductive than the grains. To further investigate the loss mechanism, losses induced by the ferrites of #A, #B, and #C were measured by placing the samples in the transmission line based permeameter. The losses shown in Fig. 64 have been normalized to the film thickness after subtracting the loss generated by the permeameter, i.e., measurements performed without insertion of the ferrite sample. Shown in Table 5, #A, #B, and #C exhibit various DC electrical conductivities. Generally, higher DC electrical conductivity leads to a higher loss at RF/Microwave
frequencies. Therefore, #C should have higher loss than #A and #B. However, the losses produced by all three samples do not appear significant from each other (Fig. 64). As mentioned in the SMM measurements, the electrical conductivity of the grain boundary is higher than the grain itself. As the deposition time increases from #A to #B to #C, the grain size also increases (Fig. 60), consequently, the grain boundary becomes less. Since the conductive grain boundary generates extra loss at high frequency, therefore, less grain boundary leads to less loss production. As a result, though the DC conductivity of #C is higher than #A and #B, the less grain boundaries presented in #C produce less loss than #A and #B at RF/microwave frequencies. Consequently, the total loss in #C is almost the same as #A and #B. It is worth mentioning that the grain boundaries might not always connect each other to form a conducting channel to increase the DC conductivity. Local closed current-conducting loops might be formed as well, as shown in Figs. 62 and 63. These closed current conducting loops will not contribute to the DC conductivity, but loss at high frequencies in a similar manner as the dielectric loss.

5.3 Conclusion

We have performed the first in situ SMM characterization of multilayer ferrite film prepared by low-temperature spin-spray processing. We discovered different electrical properties at the grain boundaries and in the grains. The grain boundary appeared to be more conductive, which might be caused by charge accumulation in the grain boundary space-charge region. The observation of excessive conductivity of the grain boundaries is in good agreement with our simulation results using a large value of $\alpha$. We also observed that larger grain size so as less grain boundaries in the sample will lead to a reduction of loss at RF/microwave frequencies. This result coincides with the measurements of the insertion loss at high frequencies.
6 Conclusions and Future Work

6.1 Conclusions

Research in new materials to further decrease the size and increase the performance of transistors and passive components is in high demand. Some of these such as 2D materials and ferrites require new methods of characterization to understand their electrical and magnetic properties. The results presented in this dissertation have further improved the understanding of a few of these materials and further improves the SMM to characterize new materials on a nanoscale level. These achievements include the following.

- Development of a numerical model of the SMM including the half wavelength resonator. Using this model, changes in SMM complex reflection coefficient $\Gamma$ due to changes in material's electrical properties such as conductivity and permittivity have been characterized.

- CVD graphene resistivity and permittivity was compared to several known materials including SiO$_2$, doped Si, and Au. Using SMM it was found that the local resistivity of the CVD graphene is more resistive than Au but less resistive than 2.0x10$^{-8}$ $\Omega$ cm (doped Si). By comparing the experimental values of the CVD graphene permittivity to that of the model is was found that CVD graphene has a relative permittivity greater than 10$^5$ below 5 GHz.

- CVD graphene defects were characterized using the SMM including defects due to oxygen plasma etching and graphene wrinkles. The graphene defects due to oxygen plasma etching was compared to Raman spectroscopy and it was found that there is a close correlation between the D/G peak ratio of Raman and the contrast between pristene graphene and partially oxygen plasma etched graphene. This leads to the conclusion that the SMM is capable of characteriz-
ing the density of graphene defects at nano-scale resolutions.

- Far-IR plasmons were shown in nano-ribbon patterned graphene. Furthermore the plasmonic resonance was shown both numerically and experimentally to be tunable by both the width of the graphene ribbons and the fermi energy level of the graphene. It was also shown that there is an effective width of the graphene ribbons that is less than the patterned width due to defects at the edge. This has potential use as far-IR/THz photo detectors at room temperature.

- Finally it was shown using SMM that for spin-spray ferrite materials the nano-scale grain boundaries are more conductive than the grains themselves. This explains the unexpectedly high Landau damping factor. Because of the highly conductive grain boundaries, at high frequencies, there are large eddy current losses.

6.2 Future Work

Future work includes further analysis of both the numerical model and calibration of the SMM to obtain direct quantified results from the measurements. This includes further expanding the SMM model to account for the physical properties of the samples including grain size and the 2D nature of graphene and other materials. Experimentally a calibration method is needed to calibrate the SMM from the short 30 cm cable to the tip of the AFM. This will allows calculations of the material's electrical properties directly from the $s_{11}$ parameter.

Further investigation of graphene defects include characterization of oxygen plasma induced defects on a few 100 nm scale including edge defects. Graphene wrinkles need to be further understood including the capacitance effects between the multiple layers of graphene. Understanding these defect modes will allow for more reliable and reproducible production of graphene devices and can be applied to other 2D materials.
Finally the large relative permittivity of graphene needs to be further investigated to answer the questions where does it come from and how it can be used to further improve electronic devices.
Figure 65: Model of SMM as a vertical electric dipole above a layered medium.

7 Appendix

7.1 Appendix A: Analytical Calculations for SMM

An analytical model was developed to describe the electric field distribution for the SMM. This was molded as a vertical electric dipole above a layered medium (Fig 65 [43]).

For this we must start with the electromagnet field to be

\[ E = E_e + E_m \] \hspace{1cm} (55)

\[ H = H_e + H_m \] \hspace{1cm} (56)

Where the electric and magnetic fields have been split into the electric field due
to the electric and magnetic components (subscripts e and m respectively) and the magnetic field due to the electric and magnetic components. Then using Maxwell’s equations we get

\[ \nabla \times \mathbf{E}_e = -j\omega \mu \mathbf{H}_e \]  
(57)

\[ \nabla \times \mathbf{H}_e = j\omega \varepsilon \mathbf{E}_e + \mathbf{J} \]  
(58)

\[ \nabla \times \mathbf{E}_m = -j\omega \mu \mathbf{H}_m - \mathbf{M} \]  
(59)

\[ \nabla \times \mathbf{H}_m = j\omega \varepsilon \mathbf{E}_m \]  
(60)

From this we can introduce the magnetic potential vector \( \mathbf{A} \)

\[ \mathbf{B}_e = \mu \mathbf{H}_e \]  
(61)

\[ \mathbf{B}_e = \nabla \times \mathbf{A} \]  
(62)

Placing this back into Eq. 57 we get

\[ \nabla \times (\mathbf{E}_e + j\omega \mathbf{A}) = 0 \]  
(63)

From here we can introduce \( \varphi \) to be the electric scalar potential so that

\[ \mathbf{E}_e + j\omega \mathbf{A} = -\nabla \varphi \]  
(64)

\[ \nabla \times \left( \frac{1}{\mu} \nabla \times \mathbf{A} \right) = \omega^2 \varepsilon \mathbf{A} - j\omega \varepsilon \nabla \varphi + \mathbf{J} \]  
(65)

In a homogeneous medium this becomes
\[ \nabla (\nabla \cdot A) - \nabla^2 A = k^2 A - j \omega \mu \varepsilon \nabla \varphi + \mu J \] (66)

where \( k^2 = \omega^2 \mu \varepsilon \). Using Lorentz Gauge where \( \nabla \cdot A + j \omega \mu \varepsilon \nabla \varphi_e = 0 \) we get

\[ \nabla^2 A + k^2 A = -\mu J \] (67)

From this we can get \( E_e \) and \( H_e \) to be

\[ E_e = -j \omega A - \nabla \varphi_e = -j \omega A + \frac{\nabla (\nabla \cdot A)}{j \omega \mu \varepsilon} \] (68)

Finding \( E_m \) and \( H_m \) is similar to the above method but to save time we can make the following substitutions

\[ E_e \leftrightarrow H_m \] (69)

\[ H_e \leftrightarrow -E_m \] (70)

\[ A \leftrightarrow F \] (71)

\[ \varepsilon \leftrightarrow \mu \] (72)

\[ \nabla^2 F + k^2 F = -\varepsilon M \] (73)

\[ H_m = -j \omega F + \frac{\nabla (\nabla \cdot F)}{j \omega \mu \varepsilon} \] (74)

\[ E_m = \frac{1}{\varepsilon} (\nabla \times F) \] (75)
The total electric and magnetic fields then look like

\[ \mathbf{E} = \mathbf{E}_e + \mathbf{E}_m = -j \omega \mathbf{A} + \frac{1}{j \omega \mu \varepsilon} \nabla (\nabla \cdot \mathbf{A}) - \frac{1}{\varepsilon} (\nabla \times \mathbf{F}) \]  

(76)

\[ \mathbf{H} = \mathbf{H}_e + \mathbf{H}_m = -j \omega \mathbf{F} + \frac{1}{j \omega \mu \varepsilon} \nabla (\nabla \cdot \mathbf{F}) + \frac{1}{\mu} (\nabla \times \mathbf{A}) \]  

(77)

From here we must solve Eq. 67 and 73. Since these equations are linear, their solutions can be expressed as a linear superposition of the fundamental solutions due to point sources

\[ \mathbf{A}(\mathbf{r}) = \mu \iiint \mathbf{J}(\mathbf{r}') \mathbf{G}(\mathbf{r}, \mathbf{r}') \, dV' \]  

(78)

\[ \mathbf{F}(\mathbf{r}) = \varepsilon \iiint \mathbf{M}(\mathbf{r}') \mathbf{G}(\mathbf{r}, \mathbf{r}') \, dV' \]  

(79)

where \( \mathbf{G}(\mathbf{r}, \mathbf{r}') \) is the fundamental solution to a point source and is referred to as the Green's function. The solution for the free-space scalar Green’s function is well known and is

\[ \mathbf{G}(\mathbf{r}, \mathbf{r}') = \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{4\pi|\mathbf{r} - \mathbf{r}'|} \]  

(80)

Using this result we can now solve for the magnetic and electric potential

\[ \mathbf{A}(\mathbf{r}) = \frac{\mu}{4\pi} \iiint \mathbf{J}(\mathbf{r}') \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \, dV' \]  

(81)

\[ \mathbf{F}(\mathbf{r}) = \frac{\varepsilon}{4\pi} \iiint \mathbf{M}(\mathbf{r}') \frac{e^{-jk|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \, dV' \]  

(82)

Substituting Eqs. 81 and 82 in Eq. 76 and 77 and simplifying we get
\[
E(\mathbf{r}) = -j\omega \mu \iiint_V \left[ G_0(\mathbf{r}, \mathbf{r}') \mathbf{J}(\mathbf{r}') + \frac{1}{k^2} \nabla G_0(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}(\mathbf{r}') \right] dV' - \iiint_V \nabla G_0(\mathbf{r}, \mathbf{r}') \times \mathbf{M}(\mathbf{r}') dV' 
\]

From here if we look only in the z direction this will simplify to

\[
E_z(r) = -j\omega \mu_0 \left( 1 + \frac{1}{k_0^2} \frac{\partial^2}{\partial z^2} \right) \frac{e^{-jkr}}{4\pi r} 
\]

If we make the substitution

\[
\frac{e^{-jkr}}{r} = \int_0^\infty \frac{k_\rho}{jk_z} J_0(k_\rho |\rho|) e^{-jkz} dk_\rho 
\]

we get

\[
E_z(r) = \frac{1}{4\pi\omega \varepsilon_0} \int_0^\infty \frac{k_\rho^3}{jk_z} J_0'(k_\rho \rho) e^{-jkz,0[z]} dk_\rho 
\]

If we shows this with the electric field reflecting off of the surface below we get

\[
E_z(r) = \frac{1}{4\pi\omega \varepsilon_0} \int_0^\infty \frac{k_\rho^3}{jk_z} J_0'(k_\rho \rho) R_E e^{-jkz,0[z]} dk_\rho 
\]

\[
R_E^{(i)} = \frac{\varepsilon_{i}k_{z,i-1} e^{jk_{z,i}z_i} + B_{i}^{(i)} e^{-jk_{z,i}z_i}}{\varepsilon_{i-1}k_{z,i} e^{jk_{z,i}z_i} - B_{i}^{(i)} e^{-jk_{z,i}z_i}} 
\]

\[
\frac{B_{i}^{(i-1)}}{A_{i}^{(i-1)}} = \frac{R_E^{(i)} - 1}{R_E^{(i)} + 1} e^{jk_{z,i-1}z_i} 
\]
7.2 Appendix B: Fabrication Process

7.2.1 Graphene Transfer

1. Spin PMMA para-Methoxy-N-methylamphetamine (PMMA) onto the front side of the copper/graphene piece for 120 seconds at 3000 RPM. The PMMA is to support the graphene for the transfer steps.

2. Oxygen plasma etch the back side of the copper at 50 watts for 1 minute to remove graphene on back side.

3. Place the copper (back side down) into a solution of water and iron(III) nitrate (0.05g/ml) for 10 to 12 hours until the copper is gone.

4. The graphene/PMMA is then lifted out of the etchant and put into DI water for 1 hour to rinse.

5. The silicon/silicon dioxide wafer is cleaned using acetone, methanol, and isopropyl alcohol then plasma etched for 60 seconds. This plasma etching makes the SiO$_2$ hydrophilic to help with the transfer.

6. The Wafer is then dipped into the DI water containing the graphene/PMMA. With the wafer gently lift the graphene/PMMA out of the DI water.

7. Place the wafer onto a hotplate at 50°C for 15 minutes. After the 15 minutes turn the temperature up to 150°C and let the wafer set for 15 minutes.

8. After the wafer has cooled for 5 minutes, rinse the PMMA off of the graphene using an acetone bath for 5 minutes.

7.2.2 Patterning Graphene Gratings

1. Spin AZ-5214 onto sample for 40 seconds at 4000 RPM.
2. Soft Bake sample for 1 minute at 90 C.

3. Expose under UV lamp with mask for 30 seconds.

4. Develop Photo Resist

5. Ash in plasma etcher for 1 minute at 50 watts.

6. Rinse with Acetone, IPA, and DI water to remove PR.

8 Publications

8.1 Journal Publications

Figure 67: Patterning graphene gratings
2. Excessive grain boundary conductivity of spin-spray deposited ferrite/non-magnetic multilayer By: Xing, Yun; Myers, J.; Obi, Ogheneyunume; et al. JOURNAL OF APPLIED PHYSICS Volume: 111 Issue: 7 Article Number: 07A512 Published: APR 1 2012

3. Scanning Microwave Microscopy Characterization of Spin-Spray-Deposited Ferrite/Nonmagnetic Films By: Xing, Yun; Myers, Joshua; Obi, Ogheneyunume; et al. JOURNAL OF ELECTRONIC MATERIALS Volume: 41 Issue: 3 Pages: 530-534 Published: MAR 2012

8.2 Conference Publications


8.3 Patent

1. Dr. Yan Zhuang, Dr. Hang Huang, Kathy Brockdorff, Joshua Myers "2D Chemical Sensor." U.S. Patent Pending.

8.4 Submitted Manuscripts

8.5 Manuscript to be Submitted


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[92] Somayyeh Rahimi, Li Tao, Sk Fahad Chowdhury, Saungeun Park, Alex Jouvray, Simon Buttress, Nalin Rupesinghe, Ken Teo and Deji Akinwande, ACS Nano 8, 10471 (2014).


