A Graphene/RF Gas Sensor

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A GRAPHENE/RF GAS SENSOR

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

by

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ABSTRACT

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Toxic chemicals have been used as chemical warfare agents since ancient times, but World War 1 saw the beginning of modern chemical proliferation. There are many methods of detecting these agents, but the combination of high sensitivity, specificity, fast response, and small form factor is difficult to achieve.

More recently, graphene has been identified as a possible sensing material for ammonia and other substances. This research documents a novel method of using graphene as a chemical sensor, utilizing a radio-frequency approach to sensing. This approach utilizes all available information from the material, such as permittivity and conductivity, instead of simply examining impedance. The development of the sensor is described in depth, as well as the theoretical models used to describe its function. Finally, the overall sensitivity to ammonia and DMMP are examined experimentally.
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For my family, both blood and found.
1 Introduction and Background

1.1 Introduction

On March 19, 2013 a suburb of Aleppo was attacked [1]. A rocket fell 300m shy of a government position, landing in a civilian neighborhood. Smoke from the rocket sickened anyone that inhaled it. Rocket attacks continued until August 2013, striking six additional areas. The source of these rockets was heavily disputed, as were the chemicals that they contained. Some eyewitness reports described a yellow cloud, others white. UN investigators were denied entry to the area by Syrian President Bashar Al-Assad, and the chain of custody of available evidence was heavily disputed [2]. Compounding the difficulty in determining what happened was the ephemeral nature of the suspected chemical agent, sarin, known by its NATO designator GB. Sarin quickly breaks down in the atmosphere due to moisture, although it is persistent in the human body. Blood tests are the preferred method of determining exposure, as isopropyl methyl phosphonic acid (IMPA), a metabolite of sarin, may be measured for up to six weeks after initial exposure[3][4]. However, with limited access to the affected populace, credibly reporting the use of chemical agents to a government body is extremely difficult.

One possible method of meeting this challenge utilizes drones to sense chemical agents. Drones do not require humans to be in harm’s way and may be deployed in a clandestine manner. Chemical agents generally gather low to the ground due to their density relative to air, but a sensor with high enough sensitivity and proven selectivity may be helpful in gathering evidence against a rogue regime or group. Unfortunately, this does little to help the victims of an immediate attack.
In 1995, a cult in Japan called Aum Shinrikyo targeted the Tokyo subway system. Although the group had manufactured a large amount of sarin, the attack itself was rushed. Plastic bags filled with a mixture of 33% liquid sarin solution were placed under seats in five commuter cars were pierced with umbrellas during the Monday morning rush hour. The slowly leaking bags allowed volatilized sarin to escape, eventually affected 15 stations. 12 people died in the attack, nearly 1000 were hospitalized, and the total number of victims was in the thousands. Many of those victims included police and first responders, who lacked appropriate personal protective equipment. The Self Defense Forces were quickly mobilized to deal with the fallout.[4–6]

1.2 Current Detection Methodology

Modern means of detecting chemical warfare agents in public locations such as train stations and airports are varied but limited. They may be split into two primary categories: point detection and continuous monitoring. Point detection sensors are portable sensors that can provide a certain amount of protection, such as monitoring tape, gas detection tubes, and photometric devices. Monitoring tape is a device wherein a photosensor analyzes a slowly incrementing roll of chemically sensitive paper. The detection tape has a relatively high sensitivity (on the order of µg/cm²), but at the cost of specificity (all of the G-series turn the paper red). Gas detection tubes are tubes with an agent inside that changes color based on the
presence and type of CW. Air is drawn through at a preset rate, and the concentration is determined by the length of the color change in the tube. Photometric devices combine an incoming gas stream with hydrogen, burn it, and then examine the resulting emission for characteristic sulfur or phosphorus emission lines. Examples of these three types of point detection sources may be found in Figure 1. Continuous monitoring devices are considered movable rather than portable, as they tend to be very large arrays of electrochemical sensors more suited to a tractor trailer than a handheld device.[4], [7] These devices tend to be military-owned due to their size and cost, and have yet to be widely adopted in the civilian space.

The sensitivity of these commercially available devices vary, as do their false positive rate. In general, high sensitivity does not correlate well with high selectivity. Given the lack of a true portable device with both high sensitivity and selectivity, we sought to create a sensitive chemical gas sensor that is selective enough to determine the presence of chemical agents in a confusing chemical background such as may be found in an airport or train station. This sensor should be low power and be able to be integrated onto an existing drone platform or handheld device. Moreover, it should be able to be used continuously over a certain period of time.

1.3 A Brief History of Chemical Weapons

Although the advent of the modern use of chemical weapons (CWs) is generally ascribed to World War 1, their use in warfare is ancient. As early as 3000 BCE, Egyptians were investigating the use of poisons[5]. In 2000 BCE, “smoke screens, toxic sleep-inducing fumes, and incendiary devices” [5] were used by Indian armies against their adversaries. In 428 BCE, Europe witnessed its first recorded use of chemical weapons as the Spartans used arsenic smoke against Athens during the Peloponnesian war. [5] The Romans expanded on the use of toxic chemicals and smoke, creating materials with choking pulmonary symptoms
similar to the modern CW phosgene in effects. The Byzantine Empire saw the development of “Greek Fire” in 668 CE, wherein a noxious mix of “resin, pitch, sulfur, naphtha or petroleum, quicklime, and saltpeter” was used during naval warfare. [5].

Toxic smoke was used throughout the Renaissance period. The Thirty Years’ War saw the use of “incendiary shells filled with sulfur, tallow, rosin, turpentine, saltpeter, and antimony.” [5] These shells were used primarily during sieges of cities by starting fires within. A variant of these incendiary shells included known poisons such as belladonna in order to create toxic fumes. The extensive use of these modified shells during the siege of Groningen resulted in the first attempt to ban chemical weapons, the Strasbourg Agreement of 1675.[4], [5]

This slow development of chemical weapons changed with the onset of World War 1. The French had developed tear gas grenades prior to the war and used them throughout the conflict, becoming the first to actively use chemical weapons. The Germans, however, were the first to create a combat-effective chemical weapon. Initial attempts used hollow rounds with various chemicals, but Fritz Haber combined these ideas and simply used common gas cylinders filled with chlorine. This technique was employed at the Second Battle of Ypres, leading to 5,000 Allied casualties[4], [5]. The success led to a chemical arms race and the introduction of phosgene, diphosgene, and eventually the dreaded mustard gas. Unlike the more transient chlorine and phosgene, mustard gas could remain in trenches for weeks. Entire platoons became casualties after resting in shell craters contaminated by mustard gas[5]. Chlorine, phosgene, and diphosgene are most dangerous through inhalation and so could be readily neutralized by the proper use of gas masks. Mustard gas, however, is classified as a blister agent. It has a high lipid solubility, which encourages ready absorption through the skin. Full-body chemical suits, introduced well after this conflict, are still the preferred means of protection.
1.4 G-Series Chemical Agents

The end of the war did not end the interest in chemical weapons, but the next step in CW development came as a surprise. Gerhard Schrader of IG Farbenindustrie was developing a new series of insecticides when he first developed tabun (GA) in 1934. He found that tabun was extremely effective against leaf lice, but unfortunately it also affected his laboratory assistants[8][4], [5]. The buildup towards the Second World War forced all military-related advancements to be reported to the Nazi government, and the development of the rest of the German series quickly followed.

GA and the rest of the G-series chemical weapons, so denoted by NATO as they were initially developed in Germany, are organophosphates or esters of phosphoric acids. In addition to nerve agents, this class of chemicals may be used as pesticides, solvents, and dispersant additives. This series of nerve agents are incredibly toxic due to their suspected ability to block the acetylcholinesterase (AChE) enzyme from breaking down. Similar medicines using this property may treat conditions such as glaucoma or postural tachycardia syndrome [9]. In the G-Series, however, this property causes acetylcholine (ACh) to accumulate at neural synapses by inhibiting cholinesterase (a neurotransmitter). Reactivation is not possible after a certain amount of time for this series, which varies based on the chemical. This process, often referred to as “aging,” is poorly understood.

Now funded by the Nazi Government, Schrader discovered the second of the G-series of nerve agents, sarin (GB), in 1938. It was far more potent as a nerve agent than tabun, and its use was quickly militarized. The actual toxicity is difficult to determine; even the office of the Army Surgeon General does not currently have an acute exposure standard.[10]

The US Army developed munitions utilizing chemical weapons, particularly GB. [13] Many countries followed suit, including Russia. Following the fall of the Soviet Union and the rise of a chemical weapons threat from terrorists, the international community created the Chemical Weapons Convention, effective in 1997[14]. Controlled and verified destruction of
chemical weapons commenced, although not all nations were signatories to this convention. For example, countries currently believed to have a stockpile of chemical weapons include North Korea and, until recently, Syria.

1.4.1 Toxicity
Much of our overall knowledge of toxicity comes from limited sources. These include the aftermath of the use of CWs, limited human testing generally performed in a military environment, and testing performed on animals. Animal testing has primarily been performed on rodents such as mice, rats, and hamsters, although it has also been performed on larger mammals such as mini pigs.

Much of our understanding of how sarin behaves is a result of the aftermath of the Tokyo chemical attacks. Victims that were treated at St. Luke’s hospital were monitored after their treatment,[17] and in multiple controlled studies, chronic effects were observed seven years after initial exposure.[18] These symptoms are varied, ranging from quantitative neurological deficiencies to indefinite complaints such as fatigue. [4] Gulf War veterans exposed to the byproducts of the destruction of or low-level exposure to chemical weapons report similar symptoms, as well as increased incidences of certain cancers.[4]

<table>
<thead>
<tr>
<th>Concentration (mg-min/m³)</th>
<th>Concentration (ppm)</th>
<th>Symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.08</td>
<td>Headache, Miosis</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>Mild Effects</td>
</tr>
<tr>
<td>25</td>
<td>4.4</td>
<td>Severe Incapacitation</td>
</tr>
<tr>
<td>35</td>
<td>6.1</td>
<td>Death (estimated)</td>
</tr>
</tbody>
</table>
A review of available toxicity data published in 1997 proposed the values available in Table 1 for exposure through inhalation. These were converted to ppm using the molecular value for sarin of 140.09 g/mol. Under these guidelines, it is thought that sarin first begins to affect the human body at a concentration of .08ppm, resulting in the physical symptoms of headaches, miosis, and rhinorrhea. These effects become more pronounced at .3ppm, including a measured decrease in the area of the pupil. Severe incapacitation follows at 4.4 ppm and a dosage of 25mg-min/m³. Death results from a concentration of 6.1 ppm and a dosage of 35 mg-min/m³.[10] Since even low exposure of sarin has the possibility of creating long-term chronic medical issues, concentrations below symptomatic exposure may already be dangerous to a human. It would be ideal, therefore, to create an early warning sensor with the ability to detect sarin at an order of 10ppb or lower.

1.4.2 DMMP

The chemical of greatest interest to this research is sarin (GB). However, due to its extreme toxicity and controlled nature, GB is not a chemical that is approved for use in research outside of government laboratories (i.e., Edgewood Chemical Biological Center or ECBC). In order to examine our sensor’s suitability as an early-warning sensor we chose a common simulant often used for these types of studies, dimethyl methylphosphonate (DMMP). DMMP is a molecule with a similar chemical structure to GB but much lower toxicity. A comparison of these molecules may be found in Figure 2. They are both organophosphorus compounds, although DMMP is missing the fluorine bond. Its primary...
use in industry is as an odor-free flame retardant. After the examination of the response to DMMP in testing at Wright State has characterized the expected response of the sensor, testing with sarin may commence at a government lab such as the ECBC.

1.4.3 Ammonia

An additional chemical of interest to this research is ammonia, a relatively common industrial chemical that is toxic to humans at certain concentrations [4]. It is also a commonly occurring chemical in the body, with research examining its utility as a stress indicator [14]. Unfortunately, ammonium nitrate is also a chemical commonly used improvised explosive devices, or IEDs [24]. Current methods of IED detection tend to be rather crude, relying primarily on robots such as the TALON (Figure 3) to find IEDs, or

![Figure 3. The US Army's TALON robot discovering an IED. [24]](image)

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![Figure 4. Navistar Defense's MaxxPro MRAP, parked next to a semi tractor trailer for size comparison. [25]](image)
heavily armored vehicles to simply drive over them, such as the US – Mine Resistant Ambush Protected Vehicles (MRAPs).

IEDs constructed using ammonium nitrate decompose gradually, releasing small amounts of ammonia into the air. Near an IED, the vapor pressure of ammonium nitrate has been found to be around 10ppb, as shown in Figure 5. Modern vapor sensors reliably detect explosives with a vapor pressure in the range of $10^2$-$10^3$ppb, far above the IED vapor concentration maximum. Due to the extreme risk to populations by terrorists or in warzones, there is great interest in creating a reliable ammonia sensor to bridge this gap.

![Figure 5](image)

Figure 5 The maximum vapor concentration of explosives in air at room temperature, reprinted from [24].
1.5 Chemical Sensing with Graphene

Graphene, a 2D hexagonal lattice of carbon atoms, was first discovered by Konstantin Novoselov and Andre Geim in 2004 [25]. They were also the first to examine its utility as a chemical sensor, by examining its reaction in the presence of ammonia as reported by Schedin [1]. They measured graphene obtained through mechanical exfoliation and transferred to an oxidized silicon wafer. A field effect transistor (FET) was created on the surface with gold contacts, as shown in the subset image in Figure 6. They measured the changes in resistivity, and found at even incredibly low dilutions of 1ppm, a change may be observed for multiple gases within a few minutes. A reprint of this first examination may be found in Figure 6. Note the changes in resistivity to ammonia (NH₃). This indicates the material is a strong candidate for use as sensing agent for a chemical sensor.

Figure 6. The changes in the resistivity of graphene over time when exposed to gases diluted to 1ppm. Ammonia has a large positive effect on the resistivity. Reprinted from [1].
Research into using graphene as a chemical sensing material proliferated. Sensitivity to chemicals such as CO, ethanol, DMMP, NO₂, and others were quickly established [a5]. Graphene was examined by Hu et al as a sensing material for DMMP in 2012 [26]. A graphic from his discussion may be found in Figure 7. Hu found that chemically reduced graphene oxide was sensitive to DMMP using a similar procedure to Schedin et al, again looking at the changes in resistivity. This came, however, at the expense of time. Although the initial response was relatively quick, the material did not appear to stabilize until almost half an hour had passed. In addition to the sensitivity to DMMP, recovery was demonstrated by heating the sample in a vacuum. After each of six treatments, the sample appeared to reach initial values.

Figure 7. An examination of the sensitivity of graphene to DMMP. Hu was able to detect DMMP at a concentration of 5ppm, over a period of a half hour. [27].
Similar examinations were also carried out by Yavari et al in examining graphene foam’s sensitivity to ammonia[27]. The graphene foam was created by growing graphene on a porous nickel foam, and then removing the nickel through chemical etchants. Yavari was able to detect ammonia with a concentration as low as 20 ppm, but again at the cost of nearly a half an hour. A figure illustrating his findings may be found in Figure 8. Like Hu, Yavari was able to demonstrate recovery of the material when heated in a vacuum.

A third examination by Hu further examined reduced graphene oxide (rGO), as a sensing medium [28]. This material is not pure graphene, but the introduction of oxygen and the dangling bonds associated with the chemically exfoliated material seemed a valid next step for examination into creating a gas sensor. The response proved quite strong and using this material Hu was able to achieve 1ppb sensitivity to ammonia, as shown in Figure 9. Similar to the previous examinations, recovery was achieved by heating the sample in a vacuum.
1.6 Sensing Approach

Most groups developing graphene into a chemical sensing material have used it in one of two ways: either as a field effect transistor (FET), or as a resistor. Both are common and valid approaches but are limited in their sensitivity. Both use DC current in order to gather information about the material. DC, however, only allows for a basic extraction of changes in resistance. By utilizing a sensor designed for high frequency electric signals, we can extract additional information such as the changes in permittivity and conductivity.

Recent work seems to support this theory. The recently reported permittivity of CVD graphene shows an extremely high value at low frequency. Given graphene’s sensitivity to DMMP and ammonia demonstrated by changes in its resistivity, it seems plausible this may carry over to its permittivity as well. By focusing our efforts on a sensor in the low GHz regime, a reliable sensor sensitive to ammonia and DMMP at 1ppb seems achievable.
1.7 Motivation, Challenges, and Objective

This work endeavors to develop an electronic sensor to detect ammonia and sarin at 1 ppb. 1 ppb was chosen for both chemicals as this is the level at which effects are observed on humans (sarin) or for the vapor pressure of the chemical found near improvised explosive devices (IEDs, ammonia). Further, this work attempts to find a route towards selectivity for these electronic devices. Proliferation of chemical weapons continues to be a concern for many governments. Detecting these chemicals before they can cause harm with a portable, low false positive rate system will ensure public safety.

Although many methods have been found to detect these chemicals, most cannot be used with high selectivity and high sensitivity at the same time. Further, most current testing methods have no additional selectivity route. This work looks to examine a potential sensing material in a new way, perhaps opening a path towards high selectivity on a single device.
2 Experiments and Procedures

2.1 Introduction

As the sensing medium for the chemical sensor, graphene is the most critical component of the device and its sourcing is equally important. A variety of methods have been developed to create graphene, and each method results in variations in the overall quality, crystal size, and electrical properties of the resultant sheet. There is a tradeoff in graphene production, as the size and quality of the graphene tends to be inversely proportional to how easily the graphene may be removed from its growth medium. Most mediums, such as copper or nickel, are not particularly useful as a substrate for an electronic device, necessitating its removal. A reliable method of removing the graphene from its growth substrate and transferring it onto a substrate suitable for testing is needed. As the sensor expands to multiple platforms, other substrates such as flexible substrates may be desired.

The manufacturing process of the device developed for the chemical sensor conforms with standard silicon processing, with the exception of a non-traditional etch method. This method was developed to protect the graphene through metallization and was found to increase the overall yield. This process will be described in more detail in Section 2.3.2.

Equally important to the sourcing of the graphene is the testing of the efficacy of the device. Initial tests were conducted simply to examine graphene’s response ammonia and DMMP, and later to optimize the device. Ammonia was examined using a small chamber filled with vapor generated from a dilution series. DMMP required a chamber and a gas flow
control scheme in order to ensure precision. Later testing was completed in a multi-gas testing chamber to ensure repeatability and reliability. This polycarbonate chamber could be completely sealed, with SMA bulkhead connections to the device and gas lines with computer-controlled valves. A LabVIEW program was created to control the gas concentration.

Other instruments outside of the primary processing and testing were required to determine graphene quality and characterize its properties. These tests included Raman spectroscopy for graphene characterization, AFM analysis to examine properties, and software material simulations using Keysight’s ADS. All masks for processing were created using layout in ADS and were manufactured by Photo-Sciences.

2.2 The Many Kinds of Graphene

Several methods have been developed to manufacture graphene, and each process has its own advantages and disadvantages. These methods include chemical vapor deposition

Figure 11. Mechanical exfoliation utilizes a thermal release tape and highly ordered pyrolytic graphite. This image is an example of mechanical exfoliation, using molybdenum disulfide (graphene would be transparent). Image Source: Graphene Supermarket. [1]
(CVD), epitaxial growth, mechanical exfoliation, and chemical exfoliation. Continuing research in each of these areas continues to improve the overall crystal size and general quality of the graphene sheet, but stark differences remain.

2.2.1 Mechanical Exfoliation
The simplest method of graphene extraction, mechanical exfoliation, was first achieved by Novosolev and Geim using Scotch tape to peel few layers of graphene from highly ordered pyrolytic graphite [29]. Mechanically exfoliated graphene has an extremely high carrier mobility of $2 \times 10^5$ cm$^2$/V/s [29], [30] and is among the purest forms known since the crystal size is derived from the graphite itself. One major drawback to this technique is the size of the flakes generated, which are on the order of 1mm. This small size limits its applications for standard wafer processing, which demands either wafer-sized sheets or graphene grown directly on a medium. The large crystallite size is extremely useful for some applications, however. The test sensor unfortunately required graphene sheets of greater than 1mm for the initial manufacturing process due to equipment limitations. For this reason, mechanical exfoliation of graphene was not considered for fabrication.

2.2.2 Epitaxial Growth

![Epitaxial Growth](image)

Figure 12 Epitaxial growth occurs when carbon crystals are desorbed from silicon carbide. This creates sheets of graphene on the surface. Image reprinted from [4].

Epitaxial growth is another method of producing graphene which relies upon silicon carbide substrates. As its name suggests, graphene film is grown by heating silicon carbide crystals in an ultrahigh vacuum to 1200-1400ºC [31],[32]. The high heat forces carbon out of the crystal and creates an ultrapure form of graphene (Figure 12). The crystal size is dependent on the
size of the silicon carbide substrate with a carrier mobility similar to that of mechanical
exfoliation. This high-quality graphene is extremely useful for high frequency transistor
applications, but the cost of silicon carbide limits the application of this type of graphene
manufacture. The cost of this method was far beyond the budget available for this project.

2.2.3 Chemical Exfoliation
Chemical exfoliation is a multi-step process, which begins with the oxidation of graphite.
This oxidation can occur in a variety of ways but is generally made using a mixture of sodium
nitrate, potassium permanganate and sulfuric acid [33]. Once oxidized, the platelets and sheets of
graphene oxide (GO) form a colloidal suspension in water [34]. The GO platelets can be split
further by sonication if necessary. This aqueous mixture allows various methods of deposition
onto substrates, including mass production methods such as printing and roll-to-roll coating. The
platelets may be further functionalized through the introduction of hydrazine or other chemicals
to create a reduced form of graphene oxide (rGO) [35].

![Figure 13. Reprinted from Loh's discussion on chemically exfoliated graphene. The top left and top right figures compare the established and the authors' model of graphene oxide. The bottom left is a transmission electron micrograph of the rGO, with an atomic model to the right. [6]](image)

The carrier mobility for this form is extremely low at around 1 cm²/V/s, although it is
tunable to some extent by using functionalized chemicals [35]. The sizes of the individual crystals
are also very small at about 10μm, which makes it unsuitable for many single-crystal devices.
Where single crystals are unnecessary, however, rGO and GO have been extremely popular to
use. Several groups have previously examined using rGO for the development of a chemical sensor [26], [36–39]. The method of use varies, but in general these chemical sensors are either resistive devices or transistor devices. In general this work appears promising, but its low carrier mobility limits its utility as a transmissive device.

2.2.4 CVD Graphene

CVD graphene is one of the more popular forms of graphene manufactured due to its relative simplicity of production, large sheet size[40], large crystal size, and carrier mobility of $10^4 \text{ cm}^2/\text{V/s} \ [41], [42]$. Graphene is created by using a sheet of metal with good carbon solubility at high temperatures, such as copper or nickel. These catalyst metals are heated to absorb carbon, and then slowly cooled. As the metals cool and the solubility is lowered, the carbon within is forced out to form crystals on the surface [41]. The result is a metal with graphene on both sides, which may then be transferred to different substrates. This process is limited only by the size of the metal sheet, meaning very large sizes are theoretically possible. Due to its high carrier mobility, large sheet size, low cost, and ease of manufacturing, CVD graphene was chosen as the primary sensing material for the chemical sensor.

Figure 14 Chemical vapor deposition allows for the creation of extremely large graphene sheets. This image is taken from Bae's effort to make a 30 inch graphene sheet [12].
2.3 Graphene Transfer

Graphene grown on a conductor is of limited utility in electronics, therefore the ability to move it to a dielectric or a semiconducting material is necessary. Several methods have been developed in order to achieve this, utilizing either polymethyl methacrylate (PMMA) [43] or a thermal release tape [40]. Once one of the graphene sheets has been coated with either the PMMA or tape, the graphene sheet on the opposite side maybe removed through oxygen plasma etching. The remaining metal growth substrate (copper for our experiment) may be removed through wet etchants. Once the graphene is free of the metal catalyst, it is a simple process to transfer it to any number of materials such as glass, silicon, or plastics. These are adhered through a heat treatment, and the remaining protective coating is removed. More recent work developed a method of adhering graphene to “rough” surfaces, i.e. metal lines and microfeatures [44], expanding the range of devices possible for fabrication.

2.3.1 Equipment

Manufacturing of the sensors took place at AFRL’s RX clean room at Wright Patterson Air Force Base in Dayton, Ohio. The equipment used included a Solitec Spinner (Model No 5100), a March Jupiter III plasma etcher (Model No. 015-3500), a Suss MJB3 Contact Mask Aligner, and a custom built thermal evaporator, sourced primarily from Denton and Kurt J. Lesker. Borrowing a clean room in this manner brought a great number of manufacturing challenges, as room conditions and maintenance could not be directly controlled. These challenges combined to make it very difficult to create a standard recipe for our process, but the general solution may be found below.
2.3.2 Procedure

For our fabrication process, a layer or a small number of layers of graphene grown on copper\(^1\) was first delicately cut to the desired size using very sharp shears. Care was taken to ensure only the absolute edges of the copper were touched by tweezers, and the copper sheet remained as flat and wrinkle-free as possible. These samples were then spin coated with PMMA at 3000 RPM for 120 seconds. The non-PMMA coated side of the samples was then carefully wiped with acetone to remove any PMMA that may have leached through to the back surface. Prior to the acetone wipe, leaching was often found on smaller samples, and samples that have been wiped have shown a reduction in trapped PMMA. They were then placed PMMA-side down in the plasma etcher, in order to remove the graphene on the unprotected side of the copper. Removal of the second layer of graphene was necessary for the copper etchant to reach the copper surface. Ineffective removal would result in copper remaining on the back of the graphene post-etch and result in a poor transfer.

The samples were exposed to oxygen plasma at 50W for 1 minute for monolayer graphene, or 2-5 minutes for multilayer graphene, depending on the number of layers. Once removed, the samples were floated copper side down, PMMA side up, in a solution of 5 grams to 100mL of iron nitrate in deionized (DI) water. The samples remained in solution for up to 24 hours, depending on the thickness of the copper foil. When copper removal was complete, the graphene was transferred to three successive dishes of DI water for 15 minutes each to clean the graphene. This was most easily done by lifting the samples using a cleaned copper screen. Often the first or second bath appeared to have a rusty color after the 15 minutes, indicating this process was in fact cleaning the graphene. Prepared graphene sheets may be stored up to a month by floating them on DI water in a sealed container.

Multiple substrates were used for this research, including standard silicon p-type wafers with 300nm of SiO\(_2\) on the surface, sapphire, and glass. Each sample was cut from its

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\(^1\) Nickel was also examined, but copper was predominantly used.
originating wafer to a sample size of 1cm x 1cm to 3cm x 3cm, depending on application. These were then cleaned by placing the samples in a bath of acetone and sonicating them for 4 minutes. They were then rinsed in isopropyl alcohol (IPA), dried with nitrogen, and placed in a plasma etcher for 1 minute at 50W with 2 bar of oxygen. In addition to cleaning the surface of remaining organic materials, this creates a hydrophilic surface, allowing for easier transference of graphene.

The prepared substrates were used to fish the graphene out of the DI water. The stack was then transferred to a hot plate where it was first heated to 60°C for 30 minutes, then to 150°C for 30 minutes. The first “soft bake” heat treatment removed the water through evaporation and allowed the graphene to come into direct contact with the substrate. The second “hard bake” heat treatment began to melt the PMMA, allowing graphene wrinkles to relax slightly and ensure good adhesion. Once the heat treatment is complete and the samples are allowed to cooled, the PMMA was removed by an acetone bath, followed by IPA. The prepared samples were stored in a dry box.

2.3.3 Optimization of Transfer Process

As the quality of graphene was critical for our research, multiple attempts to optimize the process were undertaken. This became crucial midway through the project, when our successful transfer rate dropped from nearly 100% to close to 0%. Many possible factors...
were investigated before finally determining that we had received several batches of poor quality graphene from a supplier. Examining the raw graphene samples with Raman spectroscopy indicated that there was a high degree of multilayer graphene present, as well as other contaminants. During this period, it was hypothesized that a higher temperature during bake may yield a more successful transfer mechanism. Higher temperatures had generally been avoided previously so as not to cause unwanted effects with the graphene coating material polymethyl methacrylate (PMMA).

2.3.4 Test Procedure
On the first day of processing, 20 graphene samples were cut from the copper sheet and spun with PMMA at 3000 RPM for 120 sec. By spinning an acrylic onto the desired graphene surface, the material was protected throughout the transfer process. The samples then had the non-PMMA coated surface exposed to oxygen plasma for 60 seconds at 50 W. This step removed the graphene on the back side of the copper sheet, allowing the copper growth substrate to be exposed to the copper etchant. After removal from the chamber, the samples were deposited PMMA side up in a solution of iron nitrate. The samples were floated in the solution overnight, etching the copper and ensuring a random selection of

![Image 1](image1.png)

![Image 2](image2.png)

**Figure 16. Examples of graphene transfer.** The graphene in these images are the bluish regions, and the uncovered silicon oxide is purple. The left image is of a highly successful transfer with no cuts or holes apparent in the graphene sheet. This sample was an earlier transfer that had been kept from a previous batch. The bloom in the center of the image is an artifact of the microscope, and not a hole in the graphene surface. The transfer to the right is one of the transfers conducted during the optimization experiment. Sadly, this is considered a better transfer than had been achieved in early summer. Trapped PMMA is visible to the left of the image, and regions of multilayer graphene may be found in the bottom center. Additional unknown contaminants are present.
samples in the morning. Next, a silicon wafer was cut into 20 relatively uniform samples of approximately 1.5cm x 1.5cm. These samples were cleaned chemically and stored in a dry box overnight. During chemical cleaning, all the samples were placed into a container containing acetone, and their random movement during this procedure was considered sufficiently mixed to assume a random selection.

The transfer portion of the experiment began on the second day. The graphene samples, free of their copper substrate, were transferred three successive times into fresh DI water vats. Meanwhile, the wafer samples were retrieved from the dry box and exposed to oxygen plasma for 60 seconds at 50W. This was to both give the wafers a final cleaning, and to create a hydrophilic surface on the silicon. The hydrophilic surface aids the transfer process by creating a bubble of water on the top of the substrate which facilitates the placement of graphene. The samples were then assigned a randomly selected bake time. Two samples were run at a time to minimize the total clean room usage, grouped by the hard bake time. Two graphene samples were lifted out of the DI water using silicon wafers and placed in a petri dish. The dish was set on the hot plate for 20min at the soft bake temperature. At the end of 20 minutes, the temperature was raised to the hard bake temperature. The first sample was removed after 20 minutes and allowed to cool. The second sample was removed after 40 minutes and was similarly allowed to cool. The samples were placed in separate acetone baths to remove the PMMA and cleaned according to the procedure outlined in Section 2.3.2. The hotplate was then reset to the next experiment, and the order was repeated.

Table 2 The Run Order for the experiment. Two samples were run at the same time in order to minimize total experiment time, leading to duplicates in the table.

<table>
<thead>
<tr>
<th>Soft Bake (Temp (C))</th>
<th>Time (min)</th>
<th>Hard Bake (C)</th>
<th>20</th>
<th>20</th>
<th>20</th>
<th>40</th>
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</table>
Once all the samples were complete, cleaned, and dried, they were examined under a microscope. Overview images were taken of each of the samples, and multiple zoomed images were taken at several points over the surface. These images were then processed using ImageJ, an open source image software tool developed by the NIH. The microscope used for this experiment had strong artifacts, as may be observed in Figure 16. To reduce their effect on the hue threshold, these were removed by completing a batch subtraction of the background using a simple gain image. All images were taken using the same settings in one examination, ensuring similar characteristics in all images. The images were then examined to determine a good common threshold value for the graphene, and this value was used to transform the sample images into binary black and white images. These binary images were loaded into MATLAB. MATLAB merely summed the good pixels and normalized this value to the total number of pixels, creating a comparable ratio. A routine was also created to take the valid information from the filename and load this into an array for easy examination. An example of a resultant binary image may be found in Figure 17. This sample had severe cracking, as well as numerous small holes in the graphene monolayer. Some shadowing effect from multilayer graphene may be observed.
cracking and many small holes across the surface. There were multilayer regions present, the shadow of which may be seen in some portions of the image. This array was saved as a comma-separated variable file and loaded into JMP for further examination.

Statistical analysis was used to examine the results, and the transfer parameters determined previously were found to be the optimum values. Soon after, a new supplier was found which increased our yield significantly. This was determined through multiple transfers and examining the $G'/D$ ratio using Raman spectroscopy. A brief experiment following a similar procedure to the above reverified the annealing temperature.

2.3.5 Non-Traditional Substrates

Due to the interest in wearable electronics, early work is being conducted to transfer graphene to non-traditional and flexible substrates. These include plastics, polymers, and piezoelectric materials. Successful transfers have so far been achieved on indium titanium oxide (ITO), glass, and sapphire. The procedure for both ITO and sapphire are very similar to the transfer process for silicon wafers.

![Image of graphene transferred onto borosilicate glass](image)

*Figure 18: Graphene transferred onto borosilicate glass to create single devices. The graphene is transparent on this substrate.*
2.3.6 Stacked Graphene

![Stacked graphene on sapphire. The left side of the sample has three layers of graphene with a small rectangle on top, the middle-left has two layers, the middle-right has one layer, and the far right has none. The scratch in the upper right corner is on the back side of the sapphire, and was used to ensure graphene was added to the appropriate side. A large hole is visible in one of the layers in the center, but overall good coverage was achieved. The contrast of the image has been enhanced to make the graphene more visible.](image)

Multilayer graphene may be created using chemical vapor deposition, but at greater than two layers the number of layers is difficult to control and must be verified through Raman Spectroscopy. In order to ensure a consistent stack of three or more layer graphene, it is possible to continue to process the substrate to stack additional layers of graphene on top of the first layer. This procedure remains the same with the exception of exposure of the substrate to oxygen plasma, which was omitted as it would remove the previously transferred graphene layers. These stacks may be tightly controlled, creating regions of single layer, 2-layer, 3-layer, ad infinitum. This may be useful for many different experiments.

2.4 Patterning and Manufacturing

CVD graphene transferred to silicon, glass, or sapphire is perfectly compatible with standard wafer processing. The sensors described herein have been patterned using AZ5214 and developed with MF 314. Once developed, they have been exposed to oxygen plasma at 50W for 1 minute for monolayer, and longer for multiple layers. All etches were examined optically prior to continuing fabrication. These graphene patterns are electrically isolated, and suitable for further processing.
One possible pitfall in graphene manufacturing is the metallization step. As the graphene may be doped with Au nanoparticles, we found that directly etching the substrate changed the electrical properties in uncontrollable ways. To prevent this, a “hybrid etch” was developed. After the graphene was patterned, a negative mask of the gold pattern was formed on the surface using AZ5214. The samples were then metallized with 100-200Å chromium$^2$ and 2000Å gold using thermal evaporation. This system tended to bake the photoresist, resulting in a poor liftoff. Additionally, the destructive nature of liftoff also added to loss in yield. This presented as single pads occasionally being lifted off with the gold sheet, or single spurs of gold left to short devices. If the samples were covered in a similar Cr/Au stack using thermal evaporation or sputtering and unwanted areas were removed using a positive mask and wet etchants, the graphene became heavily doped with metal particles and etch products. In order to ensure high yield, a positive mask of the gold pattern was deposited on the surface, again using AZ5214. The unnecessary gold and chromium were etched using chemical etchants, and the remaining photoresist was removed using acetone, followed by IPA. This procedure protected the graphene during the metallization step and ensured high

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$^2$ The error in the amount of chromium was due to inconsistencies in the thermal evaporator.
device yield. A summary of the various methods of etch, including hybrid etch, may be found in Figure 21.

2.5 Chemical Testing

Testing the sensor in a university environment led to several significant challenges. First, a method to reliably expose the samples to the correct concentrations of a gas needed to be determined. Secondly, an appropriate series of analogues needed to be obtained. Sarin may be tested directly at several labs, including Edgewood Chemical and Biological Center (ECBC), but Wright State University does not have the certification for this chemical. A common simulant for sarin, dimethyl methylphosphonate (DMMP), was approved for use. This chemical is still highly toxic but may be safely handled in a university setting. The second chemical used for chemical testing, ammonia, was readily sourced from the university lab.

2.5.1 Initial Testing Methodology

The initial tests were challenging in that they needed to be precise, but the materials on hand were limited. In order to maintain a high level of accuracy for both chemicals, two different approaches were used. Ammonia (NH₃) is readily soluble in water. This allows for a diluted vapor approach that may be controlled by controlling the concentration in a liquid. This led to a relatively simple testing procedure for the initial samples. DMMP,
unfortunately, is not as easy to resolve. DMMP testing was relatively consistent throughout the project, using a bubbler with nitrogen to create a saturated vapor.

2.5.1.1 Ammonia

Ammonia is readily soluble in water, allowing for a controlled concentration to be maintained using a dilution series. When added to a sealed chamber and raised to a certain temperature, the amount of ammonia in the air is proportional to the liquid concentration. This property was used to develop successive concentrations of ammonia by calculating the partial pressure at 50°C using Henry’s law:

\[
k_{H, cp} = \frac{c_a (M)}{P_g (atm)} = k^0_{H, cp} \left( \frac{1}{T} - \frac{1}{T^0} \right)
\]

For ammonia, \(k^0_{H, cp} = 60M/\text{atm}, T^0=25\degree C, C = 4000, k_{H,cp@50C} = 20M/\text{atm}\). The saturation pressure of water, the dilution agent for ammonia, is \(P_{\text{sat}} = 0.12\text{atm}\).

Table 3 Dilution series for ammonia, with the corresponding concentration of ammonia in air.
Using this, we determined the amount of ammonia needed to be dissolved in water to create the desired concentration in the vapor, as shown in Table 3. A small sealed plastic chamber was used for the testing, with a raised platform for the samples to rest on. To create the proper dilutions, 4mL of commercial NH₃-H₂O 28-30% solution was added to 100mL of distilled water. This was then successively diluted five times by taking 1mL of the previous solution and adding it to 100mL of distilled water. The testing sequence for all samples was
from lowest concentration (Dilution 5) to highest concentration (unadulterated commercial ammonia). The exposures lasted from 1-15 minutes depending on the test.

2.5.1.2 DMMP
A different method was used for controlling the DMMP concentration is similar to the method used by Edgewood Chemical and Biological Center (ECBC) to control gas concentrations. Two nitrogen-tuned mass flow controllers regulate the nitrogen inputs to a chamber. One of the carrier gas lines fed a DMMP bubbler. As it may be assumed the outflow of gas is at saturation, the total concentration is easily calculated using the equations below:

The initial DMMP system was simply readily sourced PVC pipe that was capped to create a chamber. This chamber was connected to a vacuum system using standard tubing. The vacuum was used to both remove ambient air in preparation for a nitrogen purge as well as remove any remaining DMMP after test to reduce the testers’ exposure. The DMMP concentration was controlled by opening the valve for its mass flow controller for a number of seconds. Using this, 3 seconds of flow yields 1ppb of DMMP concentration for our measurement setup.

\[ C_{DMMP}(ppm) = \frac{F_{DMMP}}{F_a + F_c + F_{DMMP}} \times 10^6 \]

\[ F_{DMMP} = \frac{P_{DMMP}}{P_o - P_{DMMP}} \times F_c \]

2.5.2 Final Testing
The experimental setup described above worked well for initial verification measurements but was not terribly robust. The dilution series was carried out with precision pipettes and clean glassware, but the error at low concentrations is particularly high.
Similarly, a more precise method of controlling the DMMP lines was desired as a non-zero error was assumed with the opening and closing of manual valves. In order to reduce error, a new testing chamber was designed.

2.5.2.1 In-Situ Chamber
The PVC chamber was difficult to open, and was difficult to calibrate for in-situ measurements. Taking what had been learned, a polycarbonate vacuum chamber with bulkhead SMA pass-through connectors and gas line connectors with stop valves was designed (Figure 25). This chamber has a volume of one cubic foot and may be completely sealed during in-situ testing. A pressure valve on the chamber indicates the rough system pressure as a failsafe.
The gas control was also redesigned. In addition to the mass flow controllers, automatic valves were added to precisely control the input. Both the mass flow controllers and the automatic valves were controlled through LabVIEW. The LabVIEW program automatically calculated the appropriate rate of the mass flow controllers for the agent gas and opened and closed the valves as needed to bring the chamber to the desired concentration using the equations described above. The program may be easily switched between ammonia and DMMP. The DMMP circuit remained the same as before, with a mass flow controller releasing nitrogen into a bubbler before mixing in the chamber. Ammonia, however, is added to the system through calibrated gas cylinders with nitrogen as the carrying gas. Similarly, a mass flow controller controlled the rate of flow of this gas as well. To maintain consistency from measurement to measurement, the system was evacuated, purged with nitrogen, and evacuated again prior to the addition of an agent gas.
Figure 26 displays a screen capture of the primary control graphical user interface. The user may input the temperature of the room, the concentration of the gas bottle or saturated DMMP, and set the max flow rate of the two mass flow controllers. The program then calculates the amount of time the valves should remain open, and the final flow rates of the controllers. An additional warning pops up if the user inadvertently selects settings that will cause the chamber to fill for more than 15 minutes, although the total time to fill the chamber is also displayed.

2.5.2.2 Ammonia
Calibrated ammonia bottles were used rather than a bubbler, reducing the possibility for error on the agent line. Multiple concentrations were purchased, from 1ppm to 1pph. Multiple bottles allowed a similar length of time for filling the chamber at multiple concentrations. All bottles were certified calibration gases. The carrier gas of all the bottles of ammonia is nitrogen.
2.5.2.3 DMMP

Similar to the initial testing phase, the DMMP required the use of a bubbler in order to create an aerosol. An MFC was used to control the nitrogen flow to the DMMP bubbler. As the MFC was calibrated for nitrogen and the air coming from the bubbler was assumed to be saturated, this is the most reliable experimental setup. The automatic stop valve to the chamber was located on the other side of the bubbler, ensuring only the desired amount of DMMP will flow to the chamber. A stainless steel bubbler was used due to the corrosive nature of DMMP.

2.5.3 Measurement and Characterization

Measurements of the devices were standard 1-port or 2-port S-Parameter measurements. On both the wafer probe station and in-situ measurements, data collected was exported as S2P files. An automatic loader program brought this information into MATLAB, and the various line parameters such as resistance, capacitance, inductance, and conductance were extracted and examined.

2.5.3.1 Wafer Probe Station

Wafer measurements were conducted using a Cascade Microtech M150 wafer probe station. Infinity GSG-150 probes were used for characterization, and an appropriate 40 GHz cable was used to connect to an Agilent PNA-L Network Analyzer (N5230C). Calibration was completed with a combination of Cascade’s wafer probe control software, WinCal, and the 101-190 calibration artifact, which is valid up to 67GHz.

2.5.3.2 In-Situ Chamber.

All measurements taken from the in-situ chamber were directly measured by a 40GHz Agilent PNA-L Network Analyzer (N5230C). The calibration was completed by Agilent’s 85033E calibration kit and the PNA’s onboard calibration software.

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3 ECBC uses a similar experimental setup
2.5.3.3 Raman Analysis
Raman analysis was used throughout the project to characterize the graphene samples used for testing. These measurements were completed using a Renishaw InVia confocal Raman microscope with a 514 nm laser. Results were analyzed using WiRE 4.1 data analysis software.

2.5.3.4 Scanning Microwave Microscopy Analysis
Scanning Microwave Microscopy (SMM) was used to characterize the local electrical properties of the graphene sheet. SMM measures the complex input reflection coefficients and was generally used for characterization purposes. The SMM used in these experiments was an Agilent 5420.

2.5.4 ADS Simulations
All masks were designed using ADS, Keysight’s (formerly Agilent’s) design system. This software enables device layout, plug and play schematic simulation, as well EM simulation using both method of moments and finite element method. One problem with this software choice was an issue of mesh size. As graphene layers are 1nm thick, the mesh was too large for most of the lab computing systems to handle. This problem was solved by simulating the overall effective permittivity of the substrate block, rather than including a 1nm thick sheet on top of the substrate.
3 The Design and Development of a Graphene RF Sensor

3.1 Introduction
The idea of using graphene as a chemical sensor isn’t particularly novel. Graphene’s discoverers published an examination of its sensitivity to chemicals in 2007 [1]. With mechanically exfoliated graphene and a Hall bar similar to that in their first Nobel prize winning experiment, they measured the changes in resistivity of graphene over time upon contact with ammonia, carbon monoxide, water, and nitrogen dioxide. This first test proved the amazing sensitivity of graphene, as they were able to detect when each individual molecule adhered to the surface. This work was then followed by further examinations into using graphene as a sensor for ammonia by Yavari [27]. He created a graphene foam which was able to achieve 20ppm sensitivity, but the measurement required 2000 seconds. One of the early examinations of graphene’s sensitivity to DMMP was not a pristine graphene sensor, but reduced graphene oxide (rGO). Hu was able to reach ppm sensitivity to DMMP using this approach, but the time required was 1000 seconds [26]. Hu later examined rGO sensitivity to ammonia and was able to reach 1ppb again using rGO. This is the first
published example of a graphene-based sensor reaching ppb sensitivity with ammonia. An example of the data from these experiments may be found in Figure 27.

3.2 DC vs RF

These early studies were able to show ppm sensitivity of both DMMP and ammonia, but at the cost of extreme amounts of time. Variations of these devices included graphene resistors and transistors, but all devices investigated have one factor in common: their reliance on DC and consequently resistivity. Resistance and resistivity, however, are not the only electrical characteristic that may be changing. By examining these materials using signals of 10MHz to 40GHz, additional parameters such as capacitance, conductance, and
inductance may be extracted, possibly expanding the sensitivity of the material. From these transmission line values changes in permittivity may be observed, which could give insight into how the sensor is truly functioning. As resistance was previously shown to be affected, it is highly probable that other electromagnetic properties may be impacted, and perhaps more dramatically.

Wu’s work implies this is true [42]. Their experiment extracted the permittivity of graphene at relatively low frequency. It appears that the permeability of CVD graphene approaches $10^6$ at relatively low frequency, and then exponentially decays, becoming more linear at 6 GHz. Using this observation, it seems likely that an RF approach to a graphene sensor will yield positive results.

3.3 Design of the Sensor

A transmission-type device was chosen early in the design process, leading to two immediate benefits. First, it is possible to increase the overall sensitivity through the use of a phase-cancellation circuit [45]. This phase cancellation circuit reduces noise through a redundant sensor as well as cancelling phase effects. Second, it becomes possible to determine more of the electrical properties of the sensor, as an entire 2-port S-parameter measurement may be taken instead of just a single port. A 2-port system makes it possible to use the transmission line equations to calculate the raw material parameters. Making the device transmissive, however, has its drawbacks. It must be matched to a $50\Omega$ characteristic impedance transmission line on both sides, and there must be enough energy transmitted through the system to detect a change. Satisfying these two requirements was one of the more difficult aspects of the initial project.

3.3.1 Initial Designs

To meet this challenge, the initial designs of the sensor were based primarily on currently-existing devices. Two of the devices were standard MEMS capacitors: an interdigital capacitor and a distributed capacitor. The interdigital capacitor contains a
capacitor on the signal line, whereas the distributed capacitor contains a capacitor between signal and ground. Two other designs chosen for initial testing were a multilayered transmission line and a metasensor or a device composed of multiple capacitors connected in serial in the signal line. These simple designs were then varied, yielding a range of arm, gap, and device lengths in order to determine the most optimal route forward. A mask featuring all of the variations was designed. The smallest features were limited by the error of the optical mask aligner to 3μm.

These initial designs were meant to maximize some feature of the transmission line, which may be considered a lumped element as shown in Figure 28. By designing for multiple features, the optimal design for maximum sensitivity to the adsorbed chemicals was found. It was also hoped that the method of sensitivity may be isolated, showing how graphene reacts to adsorbents on its surface.

![Figure 28. The standard transmission line model. This model has four components, a resistor and an inductor in series, and a capacitor and a conductor in parallel.](image)

3.3.1.1 Interdigital Capacitor

The interdigital capacitor is composed of a gold ground line and a patterned graphene signal line. The graphene signal line is broken in the center region to an “interdigital” capacitor, in which the length of the capacitor is maximized by creating a toothed cut down the center. As graphene is uniformly one atom thick, edge surface area is extremely limited for an in-line capacitor. Using a toothed channel ensures the maximal capacitive area, and
therefore the maximum capacitance for this type of device. An example of the interdigital capacitor may be found in Figure 29, as well as a table of all values of parameters used.

There were 100 total test devices on the mask for this design.

![Interdigital Capacitor Diagram](image)

Figure 29. The design of the interdigital capacitor requires two masks, one for the graphene (yellow) layer, and one for the Cr/Au (blue) layer. Variations based on the length, width and spacing between the arms were developed.

<table>
<thead>
<tr>
<th>Interdigital Capacitor</th>
<th>Width</th>
<th>Spacing</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>100</td>
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<td>500</td>
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<tr>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total Devices</strong></td>
<td></td>
<td><strong>100</strong></td>
<td></td>
</tr>
</tbody>
</table>

3.3.1.2 Distributed Capacitor

The distributed capacitor is composed of a gold signal line and two gold ground lines. Graphene arms are distributed between the signal and ground lines. The variations in this design were the graphene arms’ dimensions, including their length, their width, the spacing between the arms, and the total length of the graphene arm section (line length). A total of 96 variations were created for this device, an image and table of variations of which may be found in Figure 30. The concept behind this device is to determine whether the sensitivity is stronger in both the capacitance and conductance regions. Similar to the interdigital capacitor, this device is limited due to its in-line surface area.
3.3.1.3 Metasensor

![Diagram of distributed capacitor](image)

**Figure 30.** The distributed capacitor is composed of a graphene pattern mask (gold) and a Cr/Au mask (blue). The arm length, width, spacing, and total line length were varied according to the table on the right.

<table>
<thead>
<tr>
<th>Distribution Capacitor</th>
<th>Width</th>
<th>Spacing</th>
<th>Length</th>
<th>Line Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3</td>
<td>50</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
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<tr>
<td>20</td>
<td>20</td>
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<tr>
<td><strong>Total Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>96</strong></td>
</tr>
</tbody>
</table>

![Diagram of metasensor](image)

**Figure 31.** The metasensor is composed of a series of capacitors in the signal line patterned in graphene (yellow) and Cr/Au ground lines (blue).

The metasensor is essentially a series of capacitors, patterned from graphene with gold ground lines surrounding the pattern. This pattern had the largest degree of possible variations, and so the variety was limited due to device size. Figure 31 describes the variations in the figure, as well as the overall design. This device should have the strongest sensitivity if the capacitance is shown to have the greatest change.
3.3.1.4 Transmission Line

The transmission line design attempted to maximize the line length over a small region. Graphene ground and signal lines were interspersed and connected using a second gold layer to the appropriate launches. A third mask of hard-baked photoresist, used as a dielectric, was necessary to create this structure. This design allowed connections to the ground lines, but prevented accidental connection to the signal lines with the hard-baked photoresist between the gold lines. The variations for this design included the length of the signal lines, the spacing between the lines, and the width of the graphene lines. An example device as well as a table of the variations may be found in Figure 32. This device should prove the most sensitive if the inductance or resistance is the most strongly affected.

![Figure 32](image)

**Figure 32** The transmission line is composed of three layers, the signal and ground lines of graphene (yellow), hard baked photoresist to prevent shorts and connect the ground lines (green), and the Cr/Au ground and connection layer (blue). The width, spacing, and length of the lines was varied as shown in the table to the right. 100 total devices were generated on the mask.

<table>
<thead>
<tr>
<th>Transmission Line</th>
<th>Width</th>
<th>Spacing</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>50</td>
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<td>5</td>
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<td>500</td>
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<td>50</td>
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</tr>
</tbody>
</table>

**Total Devices =** 100

3.3.2 Initial Fabrication and Ammonia Measurements

The initial fabrication of devices yielded a mix of good and bad devices. Devices with cracks or holes in the graphene were eliminated from further testing, as well as any devices with shorted lines. The remaining devices were tested using the diluted ammonia testing procedure outlined in 2.5.2.1. During the testing, it was discovered that the chromium layer did not adhere particularly well to the graphene surface, making wafer probe measurements...
exceedingly difficult. Later versions of these devices addressed this problem by including an additional step once the negative metal photoresist pattern was developed. Prior to metallization, the devices were lightly etched with oxygen plasma for 10 seconds at 50W in order to break the bonds of the graphene slightly, while leaving most of the sheet intact. This allowed the chromium sticking layer to have more adhesion, and greatly improved both the physical and electrical contact from the gold to the graphene. Later mask designs omitted the graphene etch step entirely by ensuring the wafer probe was contacting gold on silicon, and not on graphene (Figure 33).

As later results will show, this first round of testing verified the reported results discussed earlier: that graphene may be used as an ammonia sensor. Control devices with gold patterns rather than graphene confirm the that it is graphene that is changing due to the presence of these gases, rather than any other component. How graphene is responding to the presence of ammonia will be discussed in more detail in Chapter 4.

The initial testing indicated that very few of these devices were true transmission devices as many had S12 and S21 measurements of -40dB, close to the measurement limit of the experiment. The S11 and S22 parameters, however, had a strong response and revealed sensitivity to ammonia. The characteristic impedance of the majority of the devices was also extremely low. ADS was used to attempt to understand the reasons for the low characteristic
impedance. It appeared from these simulations that graphene, when used as a transmission line, has a very tight dimension tolerance (specifically width) necessary to reach 50Ω. Given the error in our processing, this would be exceptionally difficult to achieve. Although the initial round proved graphene’s utility as a chemical sensor, the inability to tune the characteristic impedance combined with the lack of a transmissive signal drove the second iteration of devices. The initial results were closely examined to determine the path forward.

3.3.2.1 Interdigital Capacitor

The interdigital capacitor was primarily a reflective device on initial examination. Although it transmitted more power than the metasensor, none of the initial measurements indicated it could be greatly improved. Figure 34 reveals one of the devices subjected to a complete ammonia dilution series, displayed as S-Parameters. As expected for a reciprocal device, S11 and S22 matched closely, as did S12 and S21. This indicates that the device was manufactured properly and is functioning. As the maximum of the S12 and S21

Figure 34. The S-Parameter measurement from an interdigital capacitor subjected to a dilution series. Although large differences may be observed in S12 and S21, the overall energy transmitted is too low for a transmissive sensor.
measurements occurred at roughly -37dB, this cannot be considered a highly transmissive device. S11 and S22 also show the majority of the power was reflected. Nevertheless, the device had relatively high sensitivity, with an initial to saturation measurement of nearly 2dB in both S12 and S21. Although this device may prove effective in instances where a single port measurement is desired (i.e., a single probe) and wherein other parameters are not needed in order to determine specificity, that is outside the scope of this research and this device was therefore abandoned.

3.3.2.2 Distributed Capacitor

![Distributed Capacitor](image)

Figure 35 S-Parameter measurements from a distributed capacitor. The sample was measured, treated with a diluted ammonia solution, and measured again. Unlike the interdigital and the metasensor devices, the distributed capacitor had good S12 and S21 values at -1dB to -4dB. The maximum change of -1.14dB was low in comparison with other sensors.

The distributed capacitor’s initial results were similarly non-promising. Although the device was transmissive due to its gold signal line, the sensitivity to ammonia was very poor. One of the initial devices’ initial to saturation S-parameter results may be found in Figure 35.
This device also had a matched S11 and S22, as well as a matched S12 and S21. This indicates that the device was manufactured properly and is being measured correctly. The device shown had one of the larger S12/S21 sensitivities with a maximum sensitivity of .14dB. Initially, this did not seem to be one of the more promising approaches and was set aside, although it was revived later in the project.

3.3.2.3 Metasensor

![Figure 36. The S-parameter measurements for an ammonia dilution series using a metasensor. S12 and S21 were the lowest of all devices, but had the greatest and most reliable difference in S11 and S22.](image)

Although the metasensor was similarly not a transmissive device, it had the highest initial sensitivity of all devices measured. Due to this feature, much early work was devoted to this device. An example of the S-Parameters as measured from a dilution series using the metasensor may be found in Figure 36. Even at low concentrations, the sensitivity remains surprisingly high for both reflection and transmission measurements. Due to this high initial sensitivity, it was studied exhaustively over the first period of the project. Despite relative manufacturing differences, the device proved remarkably stable from sample to sample.
3.3.2.4 Transmission Line

Figure 37. S-Parameter measurements for the most successful transmission line device. The transmission line did have strong response in $S_{12}$ and $S_{21}$, but its manufacture was difficult, and the devices proved unreliable.

The transmission line held the greatest original promise and may have proven a useful foil to the metasensor. The transmission line had the greatest change in $S_{12}$ and $S_{21}$ and the most easily matched characteristic impedance. Unfortunately, the device was extremely difficult to manufacture. The hard-baked photoresist which prevented shorts proved too small to work effectively with lift-off techniques, and often devices were shorted between the two gold layers. Only two samples with an extremely limited number of devices were ever fabricated. However, due to their initial promise, a great deal of time and effort was spent attempting to create a final device composed of multiple transmission lines in parallel. This effort ultimately failed due to the difficulty of accurately predicting and designing the characteristic impedance of the device. This difficulty was mostly due to small errors in manufacturing which greatly impacted the overall characteristic impedance.
3.3.2.5 Initial Conclusions

The initial round of devices did not produce the final device, but did provide interesting insight into the method of sensitivity. It appeared capacitive structures were the most sensitive, indicating permittivity changes were likely the strongest sensing indicator. It was also confirmed that graphene could be patterned and manufactured into structures using standard silicon manufacturing techniques. Although the transferred graphene sheets had previously been examined using Raman in order to determine the overall sheet quality, these tests confirmed the graphene sheet retained its reported properties. Given the limitations of available processing, it was unlikely a properly tuned graphene line with a $50\Omega$ characteristic impedance may be manufactured. Ideally, those parameters should be dominated by the metal structure surrounding the graphene.

3.3.3 Sheet vs. Pattern

As previously stated, the ideal sensor would be a transmissive device. Using the results of multiple measurements, a simulation was created to attempt to optimize the device for transmission. After many months, no effective means was found to tune these four designs to a $50\Omega$ characteristic impedance, nor did they seem likely to transmit much energy. The very lossy designs were not ideal for low-power applications, which was also one of the original targets for this research.

After multiple failed redesigns, a simple coplanar waveguide with graphene as the dielectric material was attempted. The initial attempt was a bit of a whim, but the principle behind the idea was to embrace the issues with using graphene as a sensing medium. Although pristine graphene almost behaves as a 2D gas with incredible conductivity, the contact resistance between graphene and the chrome/gold contact is extremely high. The two contacts on either side reduce the overall transmissive energy. Viewed in this way, it seems intuitive to use the graphene sheet as a semiconductor, rather than as a conductive element.
This first test used the pattern from the distributed capacitor as well as a new pattern for rectangles of graphene. An example of the test structure may be found Figure 38, as well as its initial measurements. The initial results using an ammonia dilution series were exceptionally promising. Not only did the results prove remarkably sensitive in both transmissive and reflection measurements, but the device measurements proved comparable over multiple rounds of manufacturing and testing. Based on these results, the decision was made to move forward with the coplanar waveguide with the graphene sheet. A new mask was developed with the goal of finding the limits of sensitivity of this design, after examining the limits of the old.

Figure 38. The new coplanar waveguide designs were created using the ground and signal line patterns from the distributed capacitors (yellow) and a series of graphene rectangles (green). Initial testing revealed a highly transmissive device, but also a surprisingly sensitive one. The S-parameter measurements from one of the devices is shown on the right.

3.3.4 Optimization of the Device

In order to determine which direction to move towards with the next round of devices, an experiment was devised to quantify the range of sensitivity for the modified distributed capacitor. This was accomplished by measuring all of the devices on a single wafer before
exposing the sample to 30% ammonia vapor for 15 minutes. This had been shown in previous tests to saturate the devices, which will yield a measurement of the maximum amount of difference that may be observed. The modified distributed capacitor experienced a change for all devices at 2.6 ppm in previous experiments, and so determining maximum sensitivity was not the goal. All devices were measured again after exposure, and the maximum difference was recorded for each. A summary of the results may be found in Figure 39.

![Figure 39](image)

Figure 39. The coplanar waveguides created from the distributed capacitor were swept from 10MHz to 20GHz, and then saturated with ammonia. The devices were swept a second time, and the point of greatest range recorded. These were then plotted by device parameters, and a least-squares trendline calculated. A trend towards longer coplanar waveguides with a smaller gap between signal and ground may be observed.

Figure 39 shows a clear trend towards narrower gaps between signal and ground as well as longer coplanar waveguides may be observed. At the limit of the current device parameters, an exponential jump seemed to be occurring in width. Based upon these results, a new round of coplanar waveguides was created. These coplanar waveguides varied only in the spacing between the signal and the ground lines, and the length of the device. The width was varied from 3μm to 50μm, in order to have some overlap with the previous measurements for comparison, while the length was varied from 400μm to 9500μm. These devices were again initially measured, subjected to a 15-minute exposure of 30% ammonia vapor and then remeasured. An example measurement from this experiment may be found in Figure 40. Compared to the previous generation, the redesigned devices showed an order of magnitude increase in sensitivity range in both S12 and S21, while maintaining strong
transmission. The 9500μm length device proved to be largely unusable, as at high concentration the measurement was observed to go below the -40dB experimental threshold. These devices were removed from further examination. Examining the max difference from S12 and S21 for this dataset indicates the previous trend mostly holds, as may be observed in Figure 41. The length of the waveguide continued to have the greatest effect on the overall range of the sensor, while varying the size of the gap had a much less dramatic effect. Using this data, the first true prototype devices were designed.

Figure 40 This figure demonstrates the range of the second version of the coplanar waveguide. This is not the device with the greatest range but is an average response from the group. The sensitivity range, on average, increased by an order of magnitude over that previously observed.
3.3.5 Multi-Layer Coplanar Waveguide

Single-layer graphene is not, however, the only type of graphene available. It has been hypothesized that functionalizing the top layer, while maintaining a pristine graphene surface underneath, may allow for greater sensitivity in measurements. To determine the overall effect of multiple layers on the coplanar waveguide, three additional samples were fabricated and examined. These devices were identical to the previous single layer devices, with the exception that the graphene layer was composed of CVD grown 2-layer, 3-5 layer, and 6-8 layer graphene.

Figure 41. Plotting the S12 and S21 sensitivity vs both width of the gap and length of the coplanar waveguide continues the trend previously observed. The trend towards narrower gaps is not nearly as pronounced as the trend towards longer devices, although the drop begins to be beyond the utility of the device.

Figure 42. The trend for 2-Layer devices was clear towards longer devices, although the width results were more mixed.
3.3.5.1 2 Layer Graphene

The 2-layer graphene had a slightly lower maximum measurement than the 1-layer graphene but continued the strong trend of longer devices having greater overall range. The width was more scattered than the single layer device, showing a slight trend towards thinner gaps. In general, the sensitivity was similar to that of the single-layer graphene. An example of the S-Parameter measurements over a dilution series may be found in Figure 43, and the summary of the maximum range may be found in Figure 42.

![Figure 43. An example of the S-Parameter response from a 2-Layer device.](image)

3.3.5.2 3-5 Layer Graphene

The 3-5-layer graphene substrate continued the trend of having a higher transmission than the single layer equivalent. A probable reason for this is that between 2 layers and 3-5 layers, the electrical properties of the graphene change dramatically. As Wu described[42], graphene’s permittivity changes dramatically from 1GHz to 4GHz. However, thin layers of graphite do not show these properties. There must therefore be an inflection point in the number of layers, in which graphene’s unusual behavior begins.
to disappear, and the thin carbon sheet begins to behave as graphite. The overall sensitivity range for the sensor also dropped by ~5dB. Interestingly, at 3-5 layers of graphene the gap no longer affects the sensitivity of the measurement, as the linear fit was nearly flat. Length continues to be a strong factor, and the standard deviation for the individual lengths has decreased. An example measurement from the ammonia dilution

"Figure 44 The 3-5 graphene layer coplanar waveguide continued the trend of longer devices, higher sensitivity. The width of the gap, however, was nearly flat. The gap no longer seems to play a factor at this number of layers."
series may be found in Figure 45, and an examination of the maximum range versus width and length may be found in Figure 44.

3.3.5.3 6-8 Layer Graphene

![Graph of 6-8 Layer Graphene](image)

Figure 46 The 6-8 layer graphene sample’s greatest range value was 35dB, comparable to the 3-5 layer sample. The width had a slight slope towards the smaller values, but did not appear to be as significant as the length.

The sample with 6-8 layers of graphene had a similar maximum range value as the 3-5 layers of graphene and exhibited similar trends in both the length and width of the gap. It appeared that the length of the coplanar waveguide was the most critical factor, although the width of the gap between the signal line and the ground line had a small impact as well. An example of the dilution measurement may be found in Figure 47, and a summary of the maximum range against width and length may be found in Figure 46.
3.3.5.4 Response Time

The amount of time required to sense the chemical is also a critical metric of the utility of the sensor. If the sensor needs too much time, the sensitivity is moot as the humans nearby are already suffering ill effects. To examine this, a coplanar waveguide was placed in the chamber and exposed to increasing dilutions of ammonia. The measurements were taken at gradually increasing intervals from 10 seconds to 15 minutes. For .26 ppb, by 15 seconds the sample had reached a stable value. For 2.60 ppb, stability was reached by 30 seconds. This quick response time is much faster than has been shown so far in literature. The fact that stability can be reached is interesting as it suggests that the concentration can be directly measured through the sensor after a very short period of time.

Figure 47. A device examined with 6-8 graphene layers. The trend towards a higher initial transmission continues.
3.4 Mixed Background

Controlled laboratory experiments are useful for gathering the possible range of sensitivity, but the real world tends to be far more complex. The ammonia measurements, aside from the dry in-situ measurements, more closely modeled the real world than a typical experiment. All measurements were performed in the high humidity of the vapor chamber, which was not nitrogen purged prior to closure. Regardless, the sensor was able to detect ammonia at the ppb level. The DMMP measurements were more controlled due to safety, and were limited to nitrogen and DMMP. Additional chemicals may also may mask a signal. To examine a worst-case sensing scenario, methanol, water, and isopropanol vapor were added to both methods of sensing. These are common interference gasses, and were added at or near their maximum concentration at 1atm. By testing interference in this “worst case” scenario, the maximum sensitivity in a harsh environment was approximated. Figure 49

Figure 48. S21 measurements of an in-situ coplanar waveguide vs time. Multiple concentrations were examined. It appears the samples very quickly reach a stable value, as ten seconds was the lowest measurement value.
shows the results of one of these examinations. The complex environment did raise the theoretical detection limit for the device under test, but the overall sensitivity remained high.

![Image of graph showing sensor response to different concentrations of ammonia and DMMP in a complex environment]

**Figure 49.** Sensing selectivity tests of NH$_3$ in a complex environment that contains a mixture of 12% water vapor, 55% methanol vapor, 23% isopropanol, and 10% air. The S11 values increased.

### 3.5 Submerged

In addition to gas sensing, there are numerous examples where a wet test may prove useful. Wastewater treatment plants, for example, first break organic nitrogen into ammonia. This is reduced further to nitrate later in the process, but constant monitoring is necessary to ensure the wastewater is being treated appropriately. Inadequate treatment may lead to algal blooms and affect the health of the nearby population centers. Similarly, drinking water must be monitored for dissolved ammonia levels. According to the EPA, ammonia and chlorine may be added to create chloramines, which are used as a disinfectant for large water systems[46]. These levels must be continuously monitored in drinking water to ensure they are below EPA limits.
Further applications include monitoring ammonia in sweat. Ammonia is a known biomarker, and has been shown to be indicative of overall stress levels[47], [48]. Creating a sensor that can be worn, and is sensitive enough to pick up the relatively low levels of ammonia exuded from the body is an engineering challenge. Developing such a sensor has become an interest for many, including the military as an overall measure of health and exposure[49]. With these goals in mind, a proof of concept test to determine whether the graphene sensor may be used submerged in liquid were undertaken.

3.5.1 Metasensor

One of the longer metasensors was used for this examination. This choice was purely practical; it was far easier to manipulate a micropipette over the larger sensors than the smaller. The probes were placed on the metasensor, and drops of solution were successively added to the center of the sensor. The first drops were distilled water, and were dropped in a line perpendicular to the signal line so that the surface area of the bubble would not increase over the sensor. To test ammonia adsorption, a drop of 30% commercial ammonia solution

![Figure 50](image)

*Figure 50* A drawing of the measurement setup of the metasensor submersion test (top). Care was taken so that the surface area of the bubble did not grow between the measurements. The S11 measurement from the test is shown below. Over 2dB of change is present at 20GHz.
was added to the bubble. The precise concentration is thus difficult to determine, but is close to saturation of the sensor. A diagram showing the experimental setup, as well as the results from the examination, may be found in Figure 50. As may be observed from the figure, the metasensors are able to detect the presence of ammonia in a water solution. The magnitude experienced a -2dB change at 20GHz, suggesting a different mechanism for adsorption.

The spectrum is different from the previously measured samples, which is likely a difference due to the difference in dielectric constant between water and air. Further investigation is reserved for future work.

3.6 Recovery

Many sources indicate graphene may be cleaned by heating the sample in a vacuum or inert gas[50]. Ideally, ammonia and DMMP may be removed from the device and recovered in a less than pristine environment such as open air. Initial testing at the beginning of the project seemed to indicate 300-400°C were a good baking temperature, but at 400°C the graphene seemed to disappear on the wafer when observed under an optical microscope, although it was still electrically present.

To solve this mystery, two coplanar waveguides were identified for testing. One of the samples was saturated with ammonia vapor, and the other remained pristine. The samples were characterized both with Raman spectroscopy and measured using a wafer probe station. They were then heated for an hour on the hot plate. Both devices were measured and heated simultaneously. The measurements and heat treatments continued at 50°C intervals from 200°C to 350°C.

The unexposed sample, R259, had few working devices that matched the ammonia-exposed sample. One of these was a coplanar waveguide of width 10μm and length 800μm. This was a relatively sensitive device, although of a short length. Comparing these extensively measured devices to their response after heat treatments developed a model for how pristine graphene and graphene with adsorbed ammonia responds. For the unexposed
sample, the greatest change occurred between 250°C and 300°C. The graphene was also no longer visible under optical microscope, indicating it had likely been oxidized.

R226, the sample exposed to ammonia during a previous test, had a far different response than the unexposed sample. Initially, it appeared some degree of recovery had taken place, remaining visible even through the 300°C mark that had been catastrophic to the unexposed sample. It appears that the ammonia served to protect the graphene from oxidation, a conclusion that may also be drawn from the Raman data. The device began to oxidize like the others around 350°C, however. A summary of the electrical measurements may be found in Figure 51.

The Raman spectroscopy data followed the electrical data closely. Figure 52 examines the changes to the center of the 2D peak, expressed as a function of temperature. The exposed samples changed relatively little in comparison to the standard (pristine graphene on silicon, no further processing) and the not exposed samples. This suggests that the ammonia may have been partially passivating the graphene layers. It is possible that the non-exposed samples may have been protected by remaining PMMA or other chemicals from the initial fabrication process.

Figure 51. The unexposed coplanar waveguide (left) and ammonia exposed coplanar waveguide (right), experienced a degree of electrical change as they were heated. For the ammonia exposed sample, 300°C seemed to clean the sample the best, although the unexposed sample experienced a high degree of electrical change at that temperature.
The prototype version of the coplanar waveguide was a 1cm by 1cm version of the device. It was optimized for two different substrates, standard SiO2 and fused silica. The coplanar waveguide sensor is located on the center of the chip, and leads were designed to be soldered to an SMA bulkhead connector. Due to manufacturing limitations, the smallest gap width attempted was 20μm. During manufacturing, 100μm was the most commonly used device due to its relatively narrow gap and high yield. All variations were tuned to exhibit a characteristic impedance of 50Ω at 2GHz using ADS. An example of one of the designs with a 200μm gap may be found in Figure 53, along with its simulated characteristic frequency near 2GHz.

Figure 52 The center of the 2D peak, examined by the temperature of the sample. The exposed samples may be partially passivated by ammonia.

3.7 The Coplanar Waveguide Prototype

The prototype version of the coplanar waveguide was a 1cm by 1cm version of the device. It was optimized for two different substrates, standard SiO2 and fused silica. The coplanar waveguide sensor is located on the center of the chip, and leads were designed to be soldered to an SMA bulkhead connector. Due to manufacturing limitations, the smallest gap width attempted was 20μm. During manufacturing, 100μm was the most commonly used device due to its relatively narrow gap and high yield. All variations were tuned to exhibit a characteristic impedance of 50Ω at 2GHz using ADS. An example of one of the designs with a 200μm gap may be found in Figure 53, along with its simulated characteristic frequency near 2GHz.
3.8 Initial In-Situ Measurements

Initial experiments were performed at Wright State using the polycarbonate vacuum chamber described in Chapter 2. Both ammonia and DMMP were tested and examined in-situ. The gas flow into the chamber was controlled through mass flow controllers (MFCs) and valves connected to LabVIEW. The VNA was controlled remotely via a laptop and a network connection in simulation of the tests that were later performed at ECBC. These initial measurements once again showed 1 ppm sensitivity to ammonia and DMMP, as may be seen in Figure 54. Once its sensitivity was established, devices were manufactured in preparation for third party testing.
3.9 Conclusions

We have been able to develop an extremely sensitive chemical sensor. This sensor has demonstrated in-situ sensitivity to Ammonia, and DMMP. The sensitivity of the coplanar waveguides are linked to the size of the graphene sheets used in the coplanar waveguide. Longer sheets increase the surface area and allow for more sensitivity. A narrower width between the signal and ground line ensures any small local changes in charge results in immediate response. Additionally, the possibility of using the sensor in an underwater capacity was investigated and found to be possible. The next piece of the puzzle is to determine specificity, which seems to be linked with the response of graphene to the chemical adsorbents. The nature of this response will be investigated more fully in Chapter 4.

Figure 54. In-situ sensing results for ammonia, from 1ppm to 100ppm. As had been observed previously, saturation occurred faster than our measurement interval.
4 Graphene as a Sensing Material

4.1 Introduction

The initial design and development of the sensor was generally successful. High sensitivity was achieved with the target chemicals of ammonia and DMMP. The sensor quickly achieved saturation at various concentrations and was shown to be stable over time. In addition to this, however, several patterns emerged. It was noted that the resonant frequency of the device shifted in response to the chemicals, and occasionally the response seemed to recover, or move in the opposite direction. For example, on a very dry sample, the presence of water vapor would induce a response opposite to that of ammonia. Ammonia and DMMP also seemed to have different effects on the graphene. Although each seemed to change the resonant frequency, it changed in different ways with respect to the concentration. Finally, at ECBC, this shift in resonant frequency was confirmed (Figure 55). Under

![Phase change due to change in resonance. $\Delta f_{1/2}$ is the frequency difference between the two adjacent half wavelength resonances, identified at phase angle equal to zero.](image)

Figure 55. Phase change due to change in resonance. $\Delta f_{1/2}$ is the frequency difference between the two adjacent half wavelength resonances, identified at phase angle equal to zero.
controlled conditions, a phase change from the change in resonance was observed. What is responsible for this effect, and how it may be used for specificity, is discussed in this chapter.

4.2 Background
One of the first experiments performed by the discoverers of graphene was a simple experiment to determine its sensitivity to ammonia. [1] Mechanically exfoliated graphene was fashioned into a Hall bar using oxygen plasma. NH3, CO, H20, and NO2 were each heavily diluted by an inert carrying gas (He or N) and flowed over the graphene Hall bar. The resistivity in these measurements were found to be heavily impacted by the adsorbed gases, with changes in both the positive and negative direction.

![Graphene Resistivity Changes](image)

**Figure 56** A description of resistivity changes in graphene due to the adsorption of molecules, as described in Schedin's work with a mechanically exfoliated Hall bar. [1]

How graphene is able to respond so quickly and strongly to adsorbed gases has been the focus of much research. As a 2D material, graphene may be intrinsically optimized as a sensing agent. Its entire volume is essentially a possible active region, and the hexagonally bound carbon atoms are able to maximize any interaction with molecules near its surface. It is also unique in that it has an extremely high conductivity that approaches an electron gas. [31]
Molecules that approach the surface of graphene may be adsorbed, meaning they may become adhered to the surface of graphene. The molecule may be adhered in a variety of configurations, and each of these configurations has a corresponding energy relationship with the graphene. In addition to the binding energy, there may be a charge transfer between the adsorbed molecule and the graphene. The molecule may become either a donor or an acceptor, and therefore locally dope the graphene. This effect is essentially what Schedin et al initially observed. [1]

Multiple studies have examined the interactions between graphene and other chemicals; several reported values for adsorption energy ($E_a$), distance, and charge transfer are shown in Table 4. Examinations have been conducted both theoretically using density functional theory (DFT) and experimentally. Experimental and theoretical data indicate ammonia to be a donor molecule and water to be an acceptor. This matches our experimental measurements that seemed to indicate a reversal when a dry graphene sheet was exposed to water vapor.

Table 4 Molecule Orientations, distances above the graphene surface, absorption energy $E_a$, and charge transfer $\Delta Q$ from two studies. Both $\text{H}_2\text{O}$ and $\text{NO}_2$ are acceptors, and the other chemicals are donors.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Position</th>
<th>Orientation</th>
<th>d(A)</th>
<th>$E_a$ (meV)</th>
<th>$\Delta Q$ (e)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>C</td>
<td>v</td>
<td>3.5</td>
<td>47</td>
<td>-0.025</td>
<td>[51]</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>C</td>
<td>d</td>
<td>3.45</td>
<td>48.87</td>
<td>0.027</td>
<td>[52]</td>
</tr>
<tr>
<td>$\text{NH}_4$</td>
<td>C</td>
<td>2.19</td>
<td>644.29</td>
<td>0.54</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td>14</td>
<td>0.012</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td></td>
<td>29</td>
<td>0.018</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>$\text{NO}_2$</td>
<td></td>
<td></td>
<td>67</td>
<td>-0.099</td>
<td>[51]</td>
<td></td>
</tr>
</tbody>
</table>
Essentially, the adsorbed molecules create localized doped regions on the graphene. This is the reason why the coplanar waveguide was so successful as a sensor. By increasing the length of the waveguide, the total surface area of the sensor was maximized. However, by also minimizing the width of the gap, the effects of the doped regions were more pronounced. Figure 55 visualizes this effect. In this figure, the yellow dots represent donor molecules like ammonia, and the blue dots represent acceptor molecules like H\textsubscript{2}O. These doped regions can be thought of in terms of the transmission line model as shown in Figure 57. Capacitance may be the most affected term, as \( C = \frac{q}{V} \).

Looking at the relationships between capacitance and chemical absorption yields some insight as to what is occurring. (Redacted) shows the normalized capacitance measurements displayed by frequency. These shifts in frequency do not occur during control experiments with

Figure 58. Visualization of the effects of molecules on the surface of graphene. The blue regions represent acceptor regions of adsorbed water, and the yellow circles donor regions of adsorbed ammonia. By increasing the length, the surface area is maximized. By decreasing the width, the effects of the doped regions may be maximized.

Figure 57 The coplanar waveguide in F may be considered as a distributed transmission line. Each pocket of n or p doped graphene will result in changes in the capacitance and conductance of the transmission line.
coplanar waveguides of simply gold and silicon, and so these shifts must be related to the graphene. It was plausible that the permittivity of the graphene was being changed in some fashion related to the chemical adsorbents. As it has already been shown that adsorbed chemicals may transfer a charge to the graphene layer, this work seeks to quantify that change.

4.3 Deriving Permittivity Relationship from S-Parameters

The majority of our measurements were made using SiO2/Si wafers, with patterned graphene and gold structures. Although this was easy to manufacture, it is not a particularly easy stack to directly measure the permittivity. There is no direct relationship between permittivity and measured parameters, although it may be inferred through capacitance and conductance. The effective permittivity must be determined from the properties of all the materials beneath the signal line, and calculating an individual value is non-trivial. It is, however, the only way to determine the electrical properties of graphene in this configuration.
The goal, therefore, was to create a model to calculate the capacitance, based on predetermined values. If we know or may determine the substrate values, we ought to be able to determine the values of graphene. By then matching the capacitance of the overall structure to the simulated values, we may be able to determine the permittivity of graphene itself. The first step would be in matching the reference material to the model, and then attempting to match the graphene to the model.

Initial approaches used Keysight’s Advanced Design System (ADS). It was hoped by simulating graphene as a sheet and modifying the conductivity and permittivity, the overall effects could be examined. Unfortunately, as graphene is an extremely thin layer, ADS was not able to create a mesh given the comparatively large size of the device. Dielectric blocks with an effective permittivity were useful in narrowing the scope of the effects, but this approach proved fruitless. A more robust approach was needed.

4.3.1 The Initial Problem
The standard transmission line model includes an inductor and a resistor in series to the output. As the device contains a gold line to the output, it may be modeled as a perfectly

![Figure 60. A side view of a coplanar waveguide. The upper and lower half of the problem are split into separate Green's functions, and the remaining are recursively solved. The center conducting line is \( y=0 \), and the bottom dielectric ends at \(-b_L = \sum_{i=1}^{m} h_i \). The top dielectric ends at \( b_U = \sum_{i=1}^{m} h_i \).](image)
electrically conducting metal strip. In this case, the model may be effectively simplified to contain only the lossy capacitance and conductive elements.

This simplification leads to the following assumption:

\[ I = G \cdot V + C \cdot \frac{dV}{dt} \]

This may then be rewritten in terms of the change in charge \( Q \).

\[ \frac{dQ}{dt} = G \cdot V + C \cdot \frac{dV}{dt} \]

The time-harmonic form of this may then be observed.

\[ j\omega Q = G \cdot V + j\omega C \]

Dividing both sides by \( j\omega V \) leads to the relationship

\[ \frac{Q}{V} = C + \frac{G}{j\omega} \]

This relationship indicates that the ratio of the charge to the voltage may be used to directly measure the capacitance (real \( \left\{ \frac{Q}{V} \right\} \)) and the conductance (imag \( \left\{ \frac{Q}{V} \right\} \)).

4.3.2 The Quasi-Static Spectral Domain Analysis

The method chosen to examine the problem in this work is the spectral-domain analysis technique, first developed by Itoh and Mittra in 1974 [53] and generalized in 1978 [54]. The technique changes the space-domain integral equations into spectral-domain, allowing closed-form algebraic equations to be used. This approximation assumes the conductors used for the coplanar waveguide may be modeled as perfect electric conductors, are of zero thickness, uniform, and infinite in length. The dominant propagating mode is assumed to be quasi-TEM as the wavelengths under test are much longer than the cross-section of the waveguide. Using this
assumption, Poisson’s equation can be solved using the boundary conditions described. As will be observed, for a dielectric stack of n height, calculating the dielectric constant directly is not achievable. It is, however, possible to calculate for a range of values over a given frequency range. Finding the capacitance most closely matching the result at a specific frequency should yield the dielectric constant of the material under test.

Determining the capacitance of the device per unit length first requires a description of the electrostatic potential. As we are assuming Quasi-TEM, we may consider $\lambda \rightarrow \infty$. This indicates that we may define the relationship with the electrostatic field to a potential such that

$$E_x = -\nabla_x \varphi$$ and $\nabla^2_x \varphi = 0$. [55] This potential can then be written as:

$$\tilde{\varphi}_{E_x} = A_E e^{-\gamma' y} + B_E e^{\gamma' y}$$

$$\tilde{\varphi}_{H_z} = A_H e^{-\gamma' y} + B_H e^{\gamma' y}$$

where $\gamma'^2 = \gamma'^2 = \gamma^2 = q_n^2 - k^2$

Using this description, the electric and magnetic field equations may be characterized as:

$$\tilde{E}(q_n, y) = \hat{x} \left\{ -j \omega \mu \left[ -\gamma' A_H e^{-\gamma' y} + \gamma' B_H e^{\gamma' y} \right] \right\} + \hat{y} \left\{ q_n \omega \mu \left[ -\gamma' A_H e^{-\gamma' y} + \gamma' B_H e^{\gamma' y} \right] \right\}$$

$$+ \hat{z} \left\{ k^2 \left[ -\gamma' A_E e^{-\gamma' y} + \gamma' B_E e^{\gamma' y} \right] \right\}$$

$$\tilde{H}(q_n, y) = \hat{x} \left\{ j \omega \varepsilon \left[ -\gamma' A_E e^{-\gamma' y} + \gamma' B_E e^{\gamma' y} \right] \right\} + \hat{y} \left\{ -q_n \omega \varepsilon \left[ -\gamma' A_E e^{-\gamma' y} + \gamma' B_E e^{\gamma' y} \right] \right\}$$

$$+ \hat{z} \left\{ k^2 \left[ -\gamma' A_H e^{-\gamma' y} + \gamma' B_H e^{\gamma' y} \right] \right\}$$

For the coplanar waveguide described in Figure 60, the problem may first be split at the coplanar waveguide into upper and lower Green’s functions. A boundary condition at the interface yields the surface charge density $\rho_s$ and equates it to the normal of the electric flux
density. These are then transformed into the current $\bar{J}$ and the electric and magnetic field equations at the interface. The boundary conditions at this interface are:

$$\text{Interface } l_0 (y = 0)$$

$$E_x = E_{x,1}^L(q_n,0) = E_{x,1}^U(q_n,0)$$

$$E_z = E_{z,1}^L(q_n,0) = E_{z,1}^U(q_n,0)$$

$$\bar{H}_{x,1}^L(q_n,0) = \bar{J}_z^L$$

$$\bar{H}_{x,1}^U(q_n,0) = \bar{J}_z^U$$

$$\bar{J}_x = \bar{J}_x^L - \bar{J}_x^U$$

$$\bar{H}_{z,1}^L(q_n,0) = \bar{J}_x^L$$

$$\bar{H}_{z,1}^U(q_n,0) = \bar{J}_x^U$$

$$\bar{J}_z = \bar{J}_z^L - \bar{J}_z^U$$

$$\bar{J}_z^L = \bar{H}_{x,1}^L(q_n,0) = j \omega \varepsilon_1^L \gamma_1^L' [-A_{E,1}^L + B_{E,1}^L]$$

$$\bar{J}_z^U = \bar{H}_{x,1}^U(q_n,0) = j \omega \varepsilon_1^U \gamma_1^U' [-A_{E,1}^U + B_{E,1}^U]$$

The interface at the upper and lower edges, where $y = b_u \sum_{i=1}^{N} h_i^U$ and $y = -b_l \sum_{i=1}^{M} h_i^L$ respectively, are modeled as black bodies. For both the lower and the upper interface, the boundary conditions may be described as:

$$E_{x,M}^L = E_{z,M}^L = \bar{H}_{x,M}^L = \bar{H}_{z,M}^L = 0$$

$$\bar{E}_{x,N}^U = \bar{E}_{z,N}^U = \bar{H}_{x,N}^U = \bar{H}_{z,N}^U = 0$$
The idea behind this method is that the furthest Green’s functions may be solved, and then the results from these may be cascaded into lower Green’s functions closer to the center conductor. Each boundary represents an interface that must be handled within the cascaded functions. The boundary condition for the p\textsuperscript{th} lower interface, where p is not equal to zero, may be found below.

\[
E^L_{x,p}(q_n, y^L_p) = E^L_{x,p+1}(q_n, y^L_{p+1})
\]
\[
E^L_{z,p}(q_n, y^L_p) = E^L_{z,p+1}(q_n, y^L_{p+1})
\]
\[
\tilde{H}^L_{x,p}(q_n, y^L_p) = \tilde{H}^L_{x,p+1}(q_n, y^L_{p+1})
\]
\[
\tilde{H}^L_{z,p}(q_n, y^L_p) = \tilde{H}^L_{z,p+1}(q_n, y^L_{p+1})
\]

The same format may be followed for the upper interface, extending towards N.

\[
E^U_{x,p}(q_n, y^U_p) = E^U_{x,p+1}(q_n, y^U_{p+1})
\]
\[
\tilde{E}^U_{x,p}(q_n, y^U_p) = \tilde{E}^U_{x,p+1}(q_n, y^U_{p+1})
\]
\[
\tilde{H}^U_{x,p}(q_n, y^U_p) = \tilde{H}^U_{x,p+1}(q_n, y^U_{p+1})
\]
\[
\tilde{H}^U_{z,p}(q_n, y^U_p) = \tilde{H}^U_{z,p+1}(q_n, y^U_{p+1})
\]

Given these boundary conditions, the final form of the electric field will take the following form.

\[
E_x = E^L_{x,1}(q_n, 0) = -j \omega \mu_{i1} \left[ -\gamma^l_1 \frac{A^l_{H,1}}{B^l_{H,1}} + \gamma^l_1' \right] B^l_{H,1}
\]
\[
\tilde{E}_z = \tilde{E}^L_{z,1}(q_n, 0) = k^L_1 \left[ A^l_{E,1} + B^l_{E,1} \right] = k^L_1 \left[ 1 + \frac{A^l_{E,1}}{B^l_{E,1}} \right]
\]
This may be rewritten to solve for half of the electric and magnetic potential.

\[
B_{H,1}^L = \frac{\vec{E}_x}{-j\omega \mu_1 \gamma' \nu' \left( 1 - \frac{A_{H,1}^L}{B_{H,1}^L} \right)}
\]

\[
B_{E,1}^L = \frac{\vec{E}_z}{k_1^2 \left( 1 + \frac{A_{E,1}^L}{B_{E,1}^L} \right)}
\]

The general description of a transmission line relates the load impedance \(Z_L\) to the characteristic impedance \(Z_0\) and the reflection coefficient \(\Gamma\) by the description \(Z_L = Z_0 \frac{1+\Gamma}{1-\Gamma}\). This may be easily transformed into the admittance form \(Y_L = Y_0 \frac{1-\Gamma}{1+\Gamma}\). With this in mind, the interfaces at each of the dielectric layers may be examined. Each may be relatively simply examined as an admittance problem as shown in Figure 61. The reflection coefficient may then be written as a function of \(y\) as \(\Gamma_{E,1}^L(y) = \frac{A_{E,1}^L}{B_{E,1}^L} e^{-2\gamma' y}\). At the coplanar waveguide, the lower reflection coefficient is simply \(\Gamma_{E,1}^L(0) = \frac{A_{E,1}^L}{B_{E,1}^L}\). The upper layers follow a similar pattern as the lower, with the exception that the image is mirrored. The reflection coefficient for the upper portion may then be written as \(\Gamma_{E,U}^L(y) = \frac{B_{E,U}^L}{A_{E,U}^L} e^{2\gamma' y}\), with \(\Gamma_{E,U}^L(0) = \frac{B_{E,U}^L}{A_{E,U}^L}\).
Figure 61. The lower layers, examined as an admittance problem. The upper layers are simply a mirror of this figure.

To determine the inner admittance, then, we must first determine the electric and magnetic fields at the outer edges. These may then be used to solve the inner electric fields. These cascaded Green’s functions may then be summarized as follows:

Layer $L_p$

\[
E^L_{z,p} = k_p^L \left[ A^L_{E,p} e^{-\gamma^L_p y} + B^L_{E,p} e^{\gamma^L_p y} \right]
\]

\[
\mathcal{R}^L_{x,p} = -j \omega \varepsilon_p \gamma^L_p \left[ A^L_{E,p} e^{-\gamma^L_p y} - B^L_{E,p} e^{\gamma^L_p y} \right]
\]

Layer $L_{p+1}$

\[
E^L_{z,p+1} = k_{p+1}^L \left[ A^L_{E,p+1} e^{-\gamma^L_{p+1} y} + B^L_{E,p+1} e^{\gamma^L_{p+1} y} \right]
\]
\[ \bar{H}_{x,p+1} = -j \omega \varepsilon_{p+1} Y_{p+1}^L \left[ A_{E,p+1}^L e^{-\gamma_{p+1}^L y} - B_{E,p+1}^L e^{\gamma_{p+1}^L y} \right] \]

Layer \( U_p \)

\[ E_{z,p}^U = k_p^U \left[ A_{E,p}^U e^{-\gamma_p^U y} + B_{E,p}^U e^{\gamma_p^U y} \right] \]

\[ \bar{H}_{x,p}^U = -j \omega \varepsilon_p^U Y_p^U \left[ A_{E,p}^U e^{-\gamma_p^U y} - B_{E,p}^U e^{\gamma_p^U y} \right] \]

Layer \( U_{p+1} \)

\[ \bar{E}_{z,p+1}^U = k_{p+1}^U \left[ A_{E,p+1}^U e^{-\gamma_{p+1}^U y} + B_{E,p+1}^U e^{\gamma_{p+1}^U y} \right] \]

\[ \bar{H}_{x,p+1}^U = -j \omega \varepsilon_{p+1}^U Y_{p+1}^U \left[ A_{E,p+1}^U e^{-\gamma_{p+1}^U y} - B_{E,p+1}^U e^{\gamma_{p+1}^U y} \right] \]

Using these cascaded functions, one can progressively solve for the lower local admittance at the interface. These functions cascade using the Green’s functions outlined above. They are split into upper and lower formulas.

\[ Y_{m-p}^U = \frac{1 - \Gamma_{E,p+1}^U(y = \gamma_p^U)}{1 + \Gamma_{E,p+1}^U(y = \gamma_p^U)} \]

\[ \Gamma_{E,p}^U(y = \gamma_p^U) = \frac{Y_p^U - Y_{m-p+1}^U(y = \gamma_p^U)}{Y_p^U + Y_{m-p+1}^U(y = \gamma_p^U)} \]

\[ Y_{n-p}^L = Y_{p+1}^L \frac{1 - \Gamma_{E,p+1}^L(y = \gamma_p^L)}{1 + \Gamma_{E,p+1}^L(y = \gamma_p^L)} \]

\[ \Gamma_{E,p}^L(y = \gamma_p^L) = \frac{Y_p^L - Y_{n-p+1}^L(y = \gamma_p^L)}{Y_p^L + Y_{n-p+1}^L(y = \gamma_p^L)} \]
By combining equations and simplifying, the cascaded admittance relationship may be simplified to the following:

\[
Y_{m-p}^{U}(y = y_{p}^{U}) = Y_{p+1}^{U} \frac{Y_{m-p+1}^{U}(y = y_{p+1}^{U}) + Y_{p+1}^{U} \tanh(y_{p+1}^{U} h_{p+1}^{U})}{Y_{p+1}^{U} + Y_{m-p+1}^{U}(y = y_{p+1}^{U}) \tanh(y_{p+1}^{U} h_{p+1}^{U})}
\]

\[
Y_{n-p}^{L}(y = y_{p}^{L}) = Y_{p+1}^{L} \frac{Y_{n-p+1}^{L}(y = y_{p+1}^{L}) + Y_{p+1}^{L} \tanh(y_{p+1}^{L} h_{p+1}^{L})}{Y_{p+1}^{L} + Y_{n-p+1}^{L}(y = y_{p+1}^{L}) \tanh(y_{p+1}^{L} h_{p+1}^{L})}
\]

Now that the cascaded functions are defined, it remains only to put everything back together. The surface currents on the coplanar waveguide are related to the upper and lower contributions to the surface current.

\[
\vec{J}_x = \vec{J}_x^{U} - \vec{J}_x^{L} = G_x^{U} \vec{E}_x - G_x^{L} \vec{E}_x = G_x \vec{E}_x
\]

\[
G_x = G_x^{U} - G_x^{L} = -j \omega (Y_{n=0}^{L} + Y_{m=0}^{U})
\]

This formulation allows a direct cascaded relationship from permittivity values of the dielectric slabs to the surface currents, allowing for a calculation of the line capacitance. The result, unfortunately, is continuous over y and requires a difficult integral. In order to solve this more simply, the Galerkin method may be employed to transfer the problem into a discrete Fourier space. The Basis functions used for the method are as follows.

\[
E_{xm}(x) = \sqrt{\frac{\cos \left[ m \pi \left( \frac{x + d}{s} \right) \right]}{1 - \left[ \frac{2(x + d)}{s} \right]^2}} - \sqrt{\frac{\cos \left[ m \pi \left( \frac{x - d}{s} \right) \right]}{1 - \left[ \frac{2(x - d)}{s} \right]^2}}; m = 0,2, ...
\]

\[
+ \sqrt{\frac{\sin \left[ m \pi \left( \frac{x + d}{s} \right) \right]}{1 - \left[ \frac{2(x + d)}{s} \right]^2}} + \sqrt{\frac{\sin \left[ m \pi \left( \frac{x - d}{s} \right) \right]}{1 - \left[ \frac{2(x - d)}{s} \right]^2}}; m = 1,3, ...
\]
\[ E_{zk}(x) = \begin{cases} \cos \left[ k\pi \left( \frac{x + d}{s} \right) \right] - \cos \left[ k\pi \left( \frac{x - d}{s} \right) \right] ; k = 1,3, \ldots \\ \sqrt{1 - \left[ \frac{2(x + d)}{s} \right]^2} - \sqrt{1 - \left[ \frac{2(x - d)}{s} \right]^2} \end{cases} \]

\[ \sqrt{\sin \left[ k\pi \left( \frac{x + d}{s} \right) \right] + \sin \left[ k\pi \left( \frac{x - d}{s} \right) \right] ; k = 2,4, \ldots} \]

The Fourier transform of these basis functions are then described below.

\[ \tilde{E}_{xm}(q_n) = \begin{cases} -\frac{j\pi s}{2} \sin q_n d \left[ j_0 \left( \frac{q_n s + m\pi}{2} \right) \right] + j_0 \left( \frac{q_n s + m\pi}{2} \right) ; m = 0,2, \ldots \\ -\frac{j\pi s}{2} \cos q_n d \left[ j_0 \left( \frac{q_n s + m\pi}{2} \right) \right] - j_0 \left( \frac{q_n s + m\pi}{2} \right) ; m = 1,3, \ldots \end{cases} \]

\[ \tilde{E}_{zk}(q_n) = \begin{cases} \frac{\pi s}{2} \cos q_n d \left[ j_0 \left( \frac{q_n s + k\pi}{2} \right) \right] + j_0 \left( \frac{q_n s + k\pi}{2} \right) ; k = 1,3, \ldots \\ -\frac{\pi s}{2} \sin q_n d \left[ j_0 \left( \frac{q_n s + k\pi}{2} \right) \right] - j_0 \left( \frac{q_n s + k\pi}{2} \right) ; m = 2,4, \ldots \end{cases} \]

The Galerkin method takes the sum of the discrete m’s for its approximation. This method unfortunately includes the unknown constants c and d. The general equation for the electric field and the surface currents are found below.

\[ E_x(x) = \sum_{m=0}^{M} c_mE_{xm}(x) \]

\[ E_z(x) = \sum_{k=1}^{K} d_kE_{zk}(x) \]

\[ E_x(q_n) = \sum_{m=0}^{M} c_mE_{xm}(q_n) \]
These equations still must be solved for their $c$ values. By combining equations, it is possible to create a matrix of values, as for metallic strips $J_x$ is non-zero, and for non-metallic strips $E_x$ is non-zero. If these two are then multiplied together, the resultant equation will be equal to zero. This system is the last necessary component to create a completely scalable capacitance calculator for multiple layer dielectric coplanar waveguides.

$$
\sum_{n=1}^{\infty} \tilde{J}_x(q_n)\tilde{E}_{xi}(q_n) = 0 = \sum_{n=1}^{\infty} \sum_{m=0}^{M} [\tilde{E}_{xi}(q_n)\tilde{G}_x(q_n)\tilde{E}_{xm}(q_n)c_m]
$$

$$
0 = \sum_{n=1}^{\infty} \sum_{m=0}^{M} [\tilde{E}_{xi}(q_n)\tilde{G}_x(q_n)\tilde{E}_{xm}(q_n)c_m]
$$

$$
0 = \sum_{m=0}^{M} (p_{11}^{im}c_m); \text{ where } p_{11}^{im} = \sum_{n=1}^{\infty} \tilde{E}_{xi}(q_n)\tilde{G}_x(q_n)\tilde{E}_{xm}(q_n)
$$

$$
\sum_{n=1}^{\infty} \tilde{J}_z(q_n)\tilde{E}_{xi}(q_n) = 0 = \sum_{n=1}^{\infty} \sum_{k=0}^{K} [\tilde{E}_{zk}(q_n)\tilde{G}_z(q_n)\tilde{E}_{xj}(q_n)d_k]
$$

$$
0 = \sum_{n=1}^{\infty} \sum_{k=0}^{K} [\tilde{E}_{zk}(q_n)\tilde{G}_z(q_n)\tilde{E}_{xj}(q_n)d_k]
$$
0 = \sum_{k=0}^{K} (p_{11}^{k} d_{k}) \; \text{where} \; p_{11}^{k} = \sum_{n=1}^{\infty} E_{zk}(q_{n}) G_{z}(q_{n}) E_{xj}(q_{n})

The system of equations to be solved therefore take the form:

\begin{align*}
\text{solve for } c_{m} & \quad \begin{cases} 
p^{00}_{11} c_{0} + p^{01}_{11} c_{1} + p^{02}_{11} c_{2} + \cdots = 0 \\
p^{10}_{11} c_{0} + p^{11}_{11} c_{1} + p^{12}_{11} c_{2} + \cdots = 0 \\
p^{20}_{11} c_{0} + p^{21}_{11} c_{1} + p^{22}_{11} c_{2} + \cdots = 0 \\
\vdots \end{cases} \\
\text{solve for } d_{k} & \quad \begin{cases} 
p^{01}_{22} d_{1} + p^{02}_{22} d_{2} + p^{03}_{22} d_{3} + \cdots = 0 \\
p^{11}_{22} d_{1} + p^{12}_{22} d_{2} + p^{13}_{22} d_{3} + \cdots = 0 \\
p^{21}_{22} d_{1} + p^{22}_{22} d_{2} + p^{23}_{22} d_{3} + \cdots = 0 \\
\vdots \end{cases}
\end{align*}

4.3.3 Verification of the model

In order to test the limits of this model and determine where it is useful, a complementary model was created in Keysight’s Advanced Design System (ADS). ADS is a commonly used tool in industry that is generally accepted for design verification. The size limits of the coplanar waveguide were investigated first. In both the MATLAB model and the ADS simulation, a common silicon wafer substrate as shown in Figure 62 was developed. The width and spacing of the coplanar waveguide were scaled by a factor of 10, and the line

Figure 62. Substrate for initial testing of MATLAB model. The coplanar waveguide was modeled as a perfect conductor.
Capacitance compared over a frequency range of 10MHz to 100GHz. The results from this examination were mixed as may be found in Figure 63. Over the frequency range of 5GHz to 100GHz, the difference in line capacitance calculated by both methods had a relatively small difference. However, less than 5GHz introduced significant increases in difference.

In addition to examining the overall dimensions of the object, the permittivity and conductivity of the first layers were examined. A thin third test layer of .3µm was added just below the metal layer, and the permittivity and conductivity of this was varied. As the

Figure 63. The capacitance difference for a coplanar waveguide on a simple silicon substrate. Most were more accurate between 5GHz and 100GHz. Larger lines had greater errors.

Figure 64. The test structure modeled using both ADS and the algorithm described in this chapter. The test layer's height was 3um, and its properties were varied based on the tests described.
conductivity increased, the reliability of the algorithm decreased as may be found in Figure 65. In this figure, the ADS results are represented by a dashed line, and the Matlab results are a solid line. For materials with high conductivity, the algorithm is more accurate at higher frequency (greater than 80 GHz).

![Capacitance with Varying Conductivity](image)

Figure 65 The capacitance of a 10um transmission line modeled using both ADS and the test algorithm. A thin test layer was added to test the response of the system. For materials with high conductivity, the algorithm is valid above 80 GHz, but in general the system is well-matched.

The permittivity was also varied while holding the conductivity at a constant low value. The permittivity did not have as strong an effect as the conductivity, as may be observed in Figure 67. Given these results, we may conclude that the algorithm described in this chapter is valid for most normal materials from 10MHz to 100GHz, and with transmission line dimensions up to 1mm.
Figure 66. The permittivity of the system, as modeled by Matlab and ADS. Varying the permittivity did not cause as strong a change as the changes in conductivity.

4.3.4 Comparison with published work

The development of this model was primarily constructed using Cam Nguyen’s conformal mapping equations for common transmission lines [56] as a guide. Other available methods include Ghione and Goano’s partial capacitance method [57], as well as Yamashita’s microstrip analysis[58]. Partial capacitance initially appeared to be the most viable method of solving for permittivity, but the necessary assumptions for the approach made it unviable. The assumptions used for this approach, namely that quasi-TEM is the dominant mode and that the conductors are PEC and infinite with zero thickness, ensured that graphene could be examined as a dielectric substrate. This approach may also be used for magnetic materials.
4.3.5 Conclusions and Remarks

Keysight’s Advanced Design System (ADS) modeling environment was not initially used to model graphene due to the limits of the software. Thin materials, such as graphene, required incredibly large meshes in order to be adequately modeled. For normal materials, the measured values matched reasonably well with the simulated capacitance, as observed in Figure 67. The method described in this chapter provides a reasonable route to determining the permittivity not just of graphene on a single layer but may be expanded to extremely complex substrates with both upper and lower segments. This method may be used to develop a complete understanding of how the permittivity of graphene is changing as chemicals are absorbed.

![Capacitance graph](image)

**Figure 67** The experimental results of a coplanar waveguide, as well as its ADS simulation. The parameters match reasonably well.
5 Graphene Edges

5.1 Introduction

Graphene is in many ways a unique material. It is a 2D hexagonal lattice of carbon, with extremely high electron mobility. The material approaches a 2D electron gas, and may be modeled using the relativistic Dirac equation, using the velocity of light as the Fermi velocity. Unfortunately, its lack of an energy band gap ($E_g$) limits its overall utility. It has been previously shown that adsorbed chemicals may dope the surface to create n- and p-doped regions. Given the unusual electrical properties of graphene, there may be other methods to open a band gap.

A potential method to open the $E_g$ is through the use of graphene nanoribbons (GNRs) [31], [59], [60]. Graphene nanoribbons restrict the movement of electrons inside the sheet, changing from the 2D momentum of $k=(k_x,k_y)$ to a 1D momentum problem of $k=k_x$. This bandgap has been shown to be tunable through modifications of the ribbon width. This inversely proportional relationship has been shown to be with 1.5eV achievable at gaps of 10Å [61]. These properties have made GNRs extremely attractive for FET research. One recent example is a FET developed by Chen using a GNR with a width of 20nm [62]. Interestingly, the source of the graphene appears to impact results. One of the more common methods for creating large sheets of graphene uses chemical vapor deposition (CVD). Graphene grown using CVD can achieve extremely large sheet sizes and may be processed using relatively simple standard wafer processing techniques that are scalable to the manufacturing environment. One step in manufacturing the GNRs, however, relies on oxygen plasma after applying standard lithography techniques. Simonet looked more closely
at the graphene edges produced during the manufacturing of a FET, and noticed disorder at the edges. She hypothesized that plasma etching was creating an electrically insulating edge [63]. Bischoff conducted a review of graphene nanodevices, and found a number of means of passivating the edge, including dipping the graphene in HF [64]. The width and effects of this isolating edge were still poorly understood.

Evidence of the existence of an electrically inactive layer (EIL) near the edge of the GNRs shows up during experimentation. [59], [64–67]. The width of EIL (WEIL) has been extracted from various experiments as a fitting parameter. Abeysinghe et al. estimated the WEIL is about 12 nm based on mid-infrared plasmonic resonance adsorption spectra [65]. Han et al. reported a 50 nm wide EIL in their conductance measurements [67]. Berger et al. assumed a 230 nm WEIL to match the Hall measurements [59]. The scattered results are not unexpected, as the lack of direct measurement method of WEIL combined with a variety of graphene qualities and processing techniques. Previous work has shown the significant impact even a small change can make to the band gap opening [61]. To optimize the processing condition and thus to control the $E_g$ opening, direct characterization of WEIL with high spatial resolution is critical, specifically when mass production of GNR-based FETs is required. Raman imaging has been the primary technique to probe the EIL but is limited by its poor spatial resolution (~800 nm) [66].

In this chapter, we attempt a direct measurement of the EIL of a micropatterned graphene grating using scanning microwave microscopy (SMM). SMM is a tool which can examine the surface electrical properties on at an extremely small scale. It may be used on a variety of surfaces, but recent work has examined the grain boundaries have expanded XXX SMM has been recently applied to investigate the electrical properties and surface impedance of grain boundaries in ferrites [68], and micro-patterned graphene [69], [70]. The EIL shows a lower conductivity than CVD grown graphene (CVDG) and its width is estimated to be

89
about 0.17 µm in this work. Raman images were also collected and agree with the SMM results.

5.2 Experiments

The test samples were created using transferred monolayer CVD graphene from Graphene supermarket to both Si (250 mm)/SiO2 (300 nm)/Au (100 nm) and Si (250 mm)/SiO2 (300 nm) substrates as described in Chapter 2. The method of manufacturing the nanoribbons for both samples were identical, using AZ5214E photoresist and the photolithography equipment described in Chapter 2 to create the initial resist pattern. The grating was etched using oxygen plasma at 2 Watts for 1 minute. This process created a grating structure similar to the structure found in Figure 68. The blue hexagonal lattice represents the relatively pristine graphene on top of the substrate, and the red circles at the edge represent the edge carbon atoms. Green dangling bonds may be observed at the edges. It is the width of this section of the ribbon that we wish to investigate. To measure this width, the local conductivity of the samples were examined using an SMM (Agilent 5420) [70]. The SMM is able to achieve high spatial resolution as it is essentially an extension of atomic force microscopy (AFM). Instead of a simple topography probe, the tip is connected to a spectrum Raman measurements were completed with a Renishaw InVia confocal Raman microscope.

Figure 68 The graphene grating on a Au/SiO2/Si substrate. Normal graphene is represented with the blue hexagonal lattice, whereas the EIL is visible at the edge of the ribbon as red carbon atoms with green dangling bonds.
using a 514 nm laser. Renishaw’s WiRE 4.1 data analysis software was used to examine the resulting spectra. The baseline was determined and removed using WiRE’s “intelligent polynomial” algorithms. The characteristic peaks of graphene were fitted using a single Lorentzian peak. For the Raman 2-D images, each point corresponds to a single acquisition centered at that location on the sample.

![AFM Image](image.png)

**Figure 69** The SiO\(_2\)/Si (dark brown) substrate with a graphene test grating (gold), as observed on an AFM. The AFM measures height, and small contaminating particles may be observed (bright yellow). These particles are likely PMMA residue or photoresist.

### 5.3 Results and Discussions

An SMM uses the AFM tip as a probe to measure the complex reflection coefficients. The sharp tip creates a highly focused spatial measurement to gather a local \( \Gamma_{\text{in}} \) of the region directly beneath the probe. These measurements (Cin) are taken using a different mode in order to ensure the surface morphology has no impact. Ideally, a sample will have an extremely high \( \Gamma_{\text{in}} \) as a substrate in order to ensure high contrast. For these measurements, the sample with GNRs fabricated on the Au/Si/SiO\(_2\) stack were used. Gold is extremely reflective, resists surface oxidation, and should provide a strong contrast. Graphene will have a similarly high background, as its conductivity is roughly 106 S/m [70]. The graphene used for this experiment was measured to have a sheet resistance of around 1200 \( \Omega/\square \) through Hall measurements. An AFM image of the GNR sample may be found in Figure 69. In order to
measure the width of the EIL using this method, the EIL will need to have different EM properties from the gold substrate and the pristine graphene. By designing a sample with a relatively uniform $\Gamma_{in}$, the expected change should be optimized.

The PNA connected to the SMM was first calibrated over a range of frequencies. This calibration reduces noise and allows for a more sensitive measurement [70]. To identify the resonance, the probe was lifted to provide an air gap and a frequency scan performed. The $\lambda/2$ resonance (6.05 GHz) was identified by the phase angle of $\Gamma_{in}$ ($\theta_{in}$) approaching to $\pm \pi/2$, while the $\lambda/4$ resonances (5.84 GHz) was identified as $\theta_{in}$ approaching to $\pm \pi$ in a frequency scan when the probe was lifted in air. 2D reflection measurements were then obtained. The resultant images were filtered with a Gaussian denoising algorithm and a low-pass Fourier filter. These were used to reduce artifacts within the images. The results of this examination may be found in Figure 70. As expected, the graphene and gold have a similar response to the probe, but the edge is clearly observed. Figure 70((a) and (b)) reveal darker and brighter edge lines, respectively. This indicates the EIL has a lower magnitude of $\Gamma_{in}$ and a greater phase angle at $\lambda/2$ resonance and therefore a lower electrical conductivity than the gold substrate and pristine graphene. The $\lambda/4$ resonance shown in Figure 70((c) and (d))
confirm this, as the EIL has a stronger response in both the magnitude and phase angle of $\Gamma_{in}$ [70]. With the detection of the edge confirmed, the width was determined by taking multiple line scans across the GNRs at multiple locations and recording the width in phase angle image. The phase angle was used as the response was uniformly stronger and provided a more consistent measurement than the amplitude images. The width itself was recorded by examining the full width half maximum (FWHM) of the phase angle. The distribution of results from this examination may be found in Figure 70(e). The mean width measured using this method was 0.17 µm with the standard deviation of 0.01 µm. The distribution of the WEIL is shown in Figure 70(e). The actual width of EIL should be even smaller if the impacts of tip is considered.

The width was also examined using scanning electron microscopy (SEM). Similar to the

![Figure 71](image)

**Figure 71** Raman spectra were recorded for a portion of the GNR. A 2D image of Raman $I_D/I_G$ may be found in the bottom right with the location of the line spectra marked in orange. The line spectra (c) reveal peaks at the edges. Examining the spectra of those regions in detail reveal a small D' peak (b). The center of the graphene lines does not show this peak (a).

AFM images of Figure 69, however, the edge could not be clearly distinguished. This is not particularly surprising, as the main features of the EIL are its electrical effects and dangling chemical bonds. Given that these are the other available standard techniques for examining samples at nanometer resolution, however, it seems likely that SMM will become the more
reliable method for characterizing the EIL. The other tool that may prove useful examines the aforementioned chemical bonds, Raman microscopy.

Unfortunately, the Au substrate used for SMM is not ideal for Raman measurements. The gold substrate may raise the overall background and reduce the sensitivity, creating an inaccurate measurement and effectively hiding the defect peak [71]. To measure the edges using Raman, therefore, the second sample with GNRs fabricated on SiO$_2$/Si was used. The results of this examination may be found in Figure 71. Graphene is typically characterized using the intensity and ratios of several peaks, including the G peak (~1580 cm$^{-1}$), the D peak (~1360 cm$^{-1}$), and the 2D peak (~2700 cm$^{-1}$). The D peak is strongly associated with defects within the graphene lattice, while its absence and narrow G and 2D peaks indicate a pristine monolayer sheet. The Renishaw Raman Microscope allows the user to create 2D maps of Raman data, as shown in Figure 71(d). This map uses the normalized D peak over G peak intensity ratio ($I_D/I_G$). This ratio enhances the difference between the pristine graphene (yellow), the absence of graphene (blue), and the presence of localized defects, defined as the EIL (black). Examining the line spectra of $I_D/I_G$ as shown in Figure 71(c) reveals a strongly localized artifact at the edge of the graphene nanoribbon, and a relatively flat center ribbon. Figure 71(a) examines the local spectra from the center of the GNR. This local inspection indicates the presence of pristine monolayer graphene as it reveals an extremely narrow G and 2D peak; the D peak is barely distinguishable from the noise floor. Examining the Raman response at the edge (identified by the line spectra) reveals a small D peak Figure 71(b) and a broad 2D peak. This suggests defects in the honeycomb in the edge, likely in a combination of defects such as point defects, armchair edges, and chiral edges [72], [73]. These types of defects were created during the plasma etching process.

The plasma etching process excites oxygen using an RF source. Ultraviolet (UV) radiation is generated through this process with a sufficient energy (~9.5 eV) to break the CAC bonds of graphene (4.9 eV). This effect is localized to the edge, as the most of the
graphene is protected from the radiation by PMMA or PR. These broken bonds are likely the primary cause of the EIL [74].

Compared to Raman spectroscopy, SMM provides a new technique to probe the EIL with the advantage of high spatial resolution. Raman spectroscopy has been shown to be sensitive to the defective bond pairs in a graphene sheet, but the spatial resolution is poor. The Raman microscope used for this examination has a resolution of ~800 nm. This is due to a combination of laser spot size as well as scattering at the surface. SMM, as an extension of AFM, has a much higher resolution of around ~8nm. This allows for a more accurate measurement of the width of the EIL. Additionally, SMM is able to characterize the electrical characteristics of the EIL, resulting in a more useful measurement.

5.4 Conclusions
The EIL has been shown to be readily apparent at RF/MW frequencies using an SMM for CVD graphene etched with oxygen plasma. The average width of this was measured at multiple points and was found to be 170 ± 8 nm. It is possible the width is linked to the method of manufacturing, specifically the UV radiation during the oxygen plasma etch. The edge is readily apparent in the SMM images due to the edge defects, which caused a lower conductivity localized at the edge. This was further verified using Raman, as the edges showed a localized defect peak indicating the presence of EIL. The SMM has been shown to be a valuable tool to further characterize the EIL and investigate its width further with different etch techniques. Understanding these edge effects are essential to designing reliable GNRs to create a specific band gap.
6 Towards the Future

6.1 Introduction
Graphene is a remarkable material. Through this work, we have shown the ways this thin film may be manufactured, processed, and developed into an extremely sensitive gas sensor. It has also been shown how its electrical properties may be examined still further through developing a capacitance model for multiple layered structures. We’ve also examined the interesting edge effects present in CVD Graphene after etching with oxygen plasma and identified the width of these structures. This work has already been shown to be a success, but there is still work left to accomplish.

6.2 Manufacturing Optimization
An extensive study of the optimal method of transferring and patternning graphene has been presented in this work. These methods were developed using the materials at hand in a research clean room, but in order to create a reliable product, these processes need to be brought to scale. The most significant challenge to scale is the graphene transfer process. Fishing graphene out of a floating solution works well enough in the lab but is not reliable enough for mass production. One possible route for optimizing this is using thermal tape rather than PMMA for the protective layer. This has the advantage of not limiting the sheet size, and omits the need to try to locate the clear sample in a clear liquid, as the thermal tape may be marked. This process has been shown to work in previous work [1], and is more readily scalable.

Another process that may require additional examination is the lithography step. Currently oxygen plasma with a ± 3µm photomask has been shown to be effective, but more
advanced means of processing may become necessary as the device is further optimized and tuned. Ensuring the thin film is protected throughout the process, and yet may be removed, will continue to be a challenge. It may be preferable to investigate other photoresists, which may be less susceptible to hardening during lift-off.

Each change in the process will require requalification of the device. This step is necessary as it possible that that the PMMA and the other chemicals currently used during the manufacturing process is doping the material and having an effect on the overall sensitivity of the device. Adding an additional cleaning step by heating the device in a vacuum after manufacturing may also make the sensor may become more sensitive.

Finally, the most critical step after the manufacturing of the device is the connection to the rest of the circuit. Multiple methods such as silver paste and low temperature solder were examined and have not been presented in this work. Wire bonds appear to be the most sensible option due to the extremely thin metal and graphene layers and the relative sensitivities of each to temperature differences. Wire bonding was not examined due to clean room limitations. Other possible methods include flip-chip and edge attachment.

6.2.1 Device Optimization
Only one prototype device was manufactured and tested, but other transmission line widths may prove more stable and sensitive. A wider line was chosen primarily for manufacturing limitations rather than sensitivity. Further testing may help confirm this.

6.2.2 Sensor Testing Optimization
The current limit for the device in optimization testing is the inability to create a stable, low-concentration atmosphere in which to test the sample. For some chemicals tested, the lowest concentration achievable saturated the device and created an extremely strong signal. These results suggest the device is far more sensitive than any yet developed. Additional work needs to be completed in order to develop a chamber that can achieve extremely low
calibrated concentrations for testing. This needs to be coordinated with ECBC, as these chemicals cannot be tested elsewhere.

In addition to this, a novel method of refereeing the chamber and certifying the low concentration must be found. It is possible that the sensor may work in the parts per trillion range, far below most reliable refereeing tests.

6.2.3 A Method for Selectivity

Chapter 5 described some of the interesting aspects of graphene nanoribbons (GNRs), and noted that the band gap has been found to be tunable through the width of the ribbon. This presents an interesting path for optimization, which has not yet been investigated. We have already shown that a sheet of graphene in a transmission line is extremely sensitive to graphene by maximizing the surface area while maintaining a high sensitivity. Further, we have shown that ribbons of graphene in a transmission line are similarly sensitive. Although it is possible that we may be able to calibrate a heating method in order to determine selectivity, a more elegant solution is to combine arrays of sensors with patterned graphene nanoribbons, each tuned to a different $E_g$. This allows for immediate determination of the energy of the connection, and may resolve the selectivity of the device. This promising method should be investigated further.

Expanding upon the current work may also yield interesting avenues for expanding selectivity. By continuing testing with these devices and measuring various gases and interference gases, we may slowly develop a library of chemicals. We may be able to further expand that library by calculating the adsorption energy of various chemicals, and examining the impact on the permittivity of graphene. To perform this examination, the simulation described in Chapter 4 needs to be completed for the test device structure, at various permittivities of graphene. The substrate should also be measured in order to ensure an accurate capture of the permittivity of graphene. This is a lengthy process, but may yield an extremely useful chemical sensor.
6.3 Graphene Properties
Finally, the electrical properties of graphene and how they change based on absorbent chemicals should be examined using the permittivity calculations described in Chapter 4. A lookup table based on different substrates, transmission line dimensions, and permittivity values of graphene should be generated in order to readily measure changes in permittivity in graphene. This information will allow for the development of a graphene permittivity library based on first principles. Its completion will expand the range and utility of the sensor.

6.4 Contributions and Discoveries
The work described herein contains several important discoveries. Graphene was found to be extremely sensitive as a chemical sensor and may prove to be an interesting area of future investigation. The chemical sensor was also, at the time of testing, the most sensitive published device for ammonia and DMMP. It is likely that combining graphene as a sensing material as well as continuing to examine possible RF applications will allow for more highly sensitive sensors to be developed.

My contributions to this work include all experimental results, with the exception of those performed by ECBC. The concept of using a graphene sheet as described in 3.3.3 was also my own idea, and the final design and optimization is my own.

6.5 Concluding Remarks
Graphene is one of the most fascinating and challenging materials to work with. With its incredibly high electron mobility, it seems perfectly suited to a wide range of applications. If its manufacturing challenges can be overcome, this material may be widely used as an extremely sensitive chemical sensor.
7 References


8 Publications

8.1 Grants
Co-authored the proposal for CBD SBIR Phase II Proposal (C2-0412). (PI: H. Huang)
Co-authored the proposal for CBD SBIR Phase I Proposal (CBD14-102). (PI: H. Huang)

8.2 Patents

8.3 Publications

8.4 Conference Papers
H. Jeon, K. Brockdorf, J. Myers, F. Kumar Vishal, N.X. Sun, B. Howe and Y. Zhuang (2016) Non-reciprocal magnetostatic surface wave propagation in a 20 nm thick single crystalline yttrium iron garnet film


