THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF ENGINEERING SCIENCE AND MECHANICS

A STUDY OF THE SPIN-DICKE EFFECT WITHIN INORGANIC SEMICONDUCTOR DEVICES

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ABSTRACT

The Spin-Dicke effect is a phenomenon already observed in electrically detected magnetic resonance (EDMR) of organic devices. The EDMR effect involves changing electron spin-states to control a recombination current. In the Spin-Dicke phenomenon, the oscillating field, $B_{1,}$ which causes resonance and changing spin-states, is approximately equal to the quasi-static magnetic field, B_0. In these experiments, the EDMR effect under the Spin-Dicke regime was observed in inorganic semiconductor devices (SiC p-n junctions) via spin-dependent recombination.

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ACKNOWLEDGEMENTS

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Chapter 1

Introduction

1.1) Motivation

Magnetoresistance is the change of resistance in a material due to an external magnetic field. Discovered in 1856, today magnetoresistance has become an interesting topic with the rise of electronic devices that utilize electron spin, or spintronics. Topics such as Organic Magnetoresistance or Giant Magnetoresistance, which won the Nobel Prize in 2007, are areas of great interest in semiconductor devices. [1]

In principle, this magnetoresistance effect can be used to analyze semiconductor devices. This phenomenon utilizes the energy splitting of electrons within a magnetic field. The magnetoresistance phenomena are closely related to electrically detected magnetic resonance (EDMR). This is especially important as these defect states can inhibit device performance. By utilizing these resonance techniques and determining the type and number of defects, the process step that could introduce these defects could be isolated and prevented. This is a major application of magnetoresistance that is often used in Dr. Lenahan's Semiconductor Spectroscopy Lab.

The magnetoresistance effect isn't only used for analysis purposes. The Lenahan group is also collaborating with Dr. Corey Cochrane's group at the Cal-Tech Jet Propulsion laboratory.

Dr. Cochrane is developing magnetic field sensors for deep space applications based on magnetoresistance phenomena. The sensitivity of the spectrometers depends upon the breadth and intensity of the magnetoresistance response. Understanding the physics behind magnetoresistance will potentially help understand the responses from these spectrometers. The devices that would be used in these expeditions would be p-n junctions, not much different from the devices I worked on for my thesis project.

1.2) Problem Statement

While magnetoresistance has been inspected greatly in organic devices, in my experiments I wanted to investigate a specific magnetoresistance effect in inorganic devices that has only been observed in organic LEDs. Specifically, I wanted to investigate the Spin-Dicke effect in SiC p-n junctions. Understanding magnetoresistance effects in inorganic devices could influence the future of analysis and applications of these devices. For example, the analysis technique I am using will be a specific form of electrically detected magnetic resonance (EDMR), known as Ultra Low-Field EDMR, where resonance occurs at only a few Gauss. Resonance preformed at these extremely low magnetic fields are very rare, and understanding physical effects like the Spin-Dicke effect will allow a greater understanding and help resolve and explain physical effects that may occur when certain physical conditions of the surroundings of electronic devices are met.

Chapter 2

Background and Literature Review

2.1) Semiconductors and the p-n Junction

2.1.1) Semiconductor Devices

Semiconductor devices are key elements for the majority of electronic systems. The devices are created using semiconductor materials, which are named that way due to having properties between a metal and an insulator. These materials have bandgaps, or an area where electrons cannot exist above near the energy if you were to fill all of the states below with available electrons around 0.25 eV to 2.5 eV. Since metals don't have a bandgap, electrons are allowed to move around the material easily with just a small amount of energy exciting it into an open energy level. Insulators have a much larger bandgap, which means the electrons are confined to their energy levels and cannot migrate around the material. Since semiconductors exist in between insulators and metals, the number of charge carriers can be increased or decreased by changing the material and the environment of the material. Increasing the temperature, for example, will allow electrons to gain enough energy from the lattice vibrations to move above the bandgap, producing an electron that can move around that energy band, and create a vacancy for electrons below the bandgap to flow into. This vacancy can be called a hole, and be treated as a pseudo-particle with a positive charge.

Semiconducting materials can also be processed in a way to introduce a larger number of holes or electrons above a small temperature. This process is known as doping. By doping a material, elements are introduced into the lattice that will produce an electron that is easily excited into the area above the energy band, known as the conduction band, or will take an electron from below the energy band, creating a hole in the so called valance band. This way, semiconducting materials can be produced that have majority carriers of electrons or holes, known as n-type and p-type materials, respectively. Utilizing these types of materials in different geometries allows for powerful circuit elements, such as sensors, voltage sources, switches, and rectifiers. The simplest semiconductor device is known as a p-n junction and is created by connecting a p-type material and an n-type material together [2].

2.1.2) P-n junction and magnetoresistance

The p-n junction is a special device that is commonly referred to as a diode. This device allows current to flow in one direction only. As there are a large number of electrons in the n-type material and large number of holes in the p-type, the electrons will want to travel over to the p-type material when a voltage is applied and holes will move the opposite direction. This causes the current to move in the direction of the holes and opposite of the electrons due to the opposite nature of the particle’s charges. The p-n junction can be used in materials as a rectifier, something to produce light, and a magnetometer, among other things. Understanding the magnetoresistance of these devices will help with the understanding of the magnetometer property, but will also help with the electrical characteristics of the materials[3].

Semiconductors are limited in performance by states known as defects, which are abnormalities in the lattice that can cause electrons to become trapped as they travel. One common way to understand these defects is by using magnetic resonance techniques in order to determine the type and quantity of these defects. Understanding the magnetoresistance of these devices can help understand the defect related responses of these magnetic resonance scans, and using different types of these magnetic resonance scans can help gain more information that will aid the understanding of magnetic resonance responses [4].

2.2) Electron Resonance Techniques

2.2.1) Electrically Detected Magnetic Resonance and ESR

The magnetic resonance technique that I was experimenting with was a form of Electrically Detected Magnetic Resonance (EDMR). This technique is based off of Electron Spin Resonance (ESR) but differs in a few aspects. These resonance methods are both derived from satisfying the resonance conditions caused by the Zeeman effect. This effect is shown in Figure 1. The Zeeman effect is the splitting of the electron spectral lines when under the influence of a high magnetic field. For example, a free electron will either have a spin of +½ or -½, corresponding to facing against or with the field. If the magnetic dipole is facing in the same direction as the magnetic field, the energy in that state will decrease as the magnetic field increases and the energy of the state facing against the magnetic field will increase [5]. These change in energies are actually proportional to the field applied demonstrated by the following equation:

$$\Delta E = g_e \mu_B B_0 \quad (1)$$

where B_0 is the external field, μ_B is the Bohr Magneton, and g_e is the g-value of the system (2.0023 for the free electron). In order for resonance to occur, the splitting distance between these lines must be equal to the energy imparted by an oscillating field that is perpendicular to the external field. The energy caused by an oscillating magnetic field is

$$\Delta E = h\nu \quad (2)$$

where h is the Planck constant and ν is the frequency of oscillation. This results in a very simple equation when resonance is satisfied:

$$g_e \mu_B B_0 = h\nu \quad (3)$$

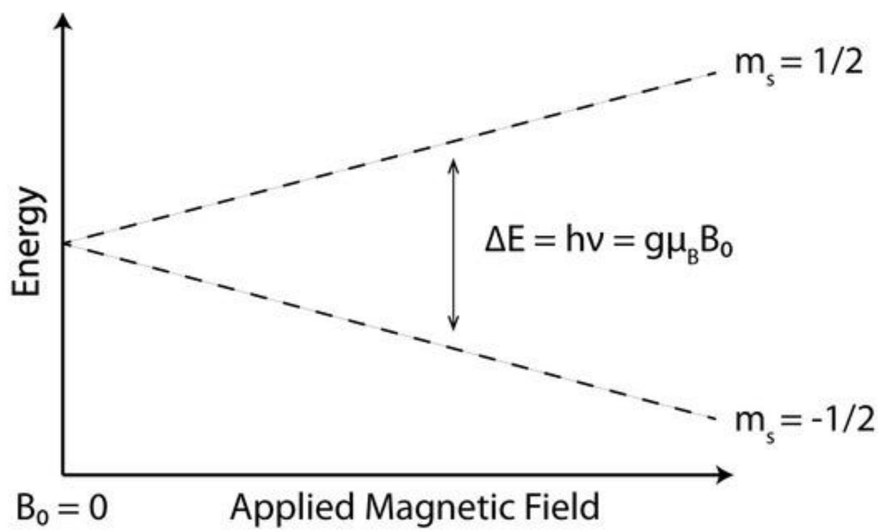

Figure 1: The Zeeman Effect [5]

Since μ_B and the h are both constants, we can then create an experiment in order to find g_e, and thus information about the material parameters we are working with. While keeping the magnetic field constant and sweeping the frequency of the oscillating signal would work, it isn't experimentally as feasible as keeping the frequency constant and just increasing the external field. The way that resonance is determined and documented is the first and main difference between EDMR and ESR. ESR will measure the reflected power from an incident microwave, where a drop in reflected power corresponds to a spike in absorbed power at resonance. EDMR utilizes an oscillating magnetic field and instead measures the change in current within the device while a bias is applied. The process through this occurs is known as spin dependent recombination as shown below [6]. The example we will use below is that the defect site is a dangling silicon bond, which is a common bond found in SiC when an oxide is grown on the material [7]. Dangling bonds will have an open state inside the bandgap that is shared by another electron with the opposite spin. If an electron approaches the defect with the same spin as the electron inside the dangling bond, the Pauli Exclusion Principle forbids the electron to drop into the deep defect. However, if a microwave or an oscillating field is applied then enough energy could be imparted to flip the spin of the electron in the dangling bond, allowing the electron to drop into the deep defect. At this point a hole from below in the valence band can then fall into the deep defect and cause a recombination current. This process can be seen in Figure 2. The change of current is then monitored in order to give information about the system [4].

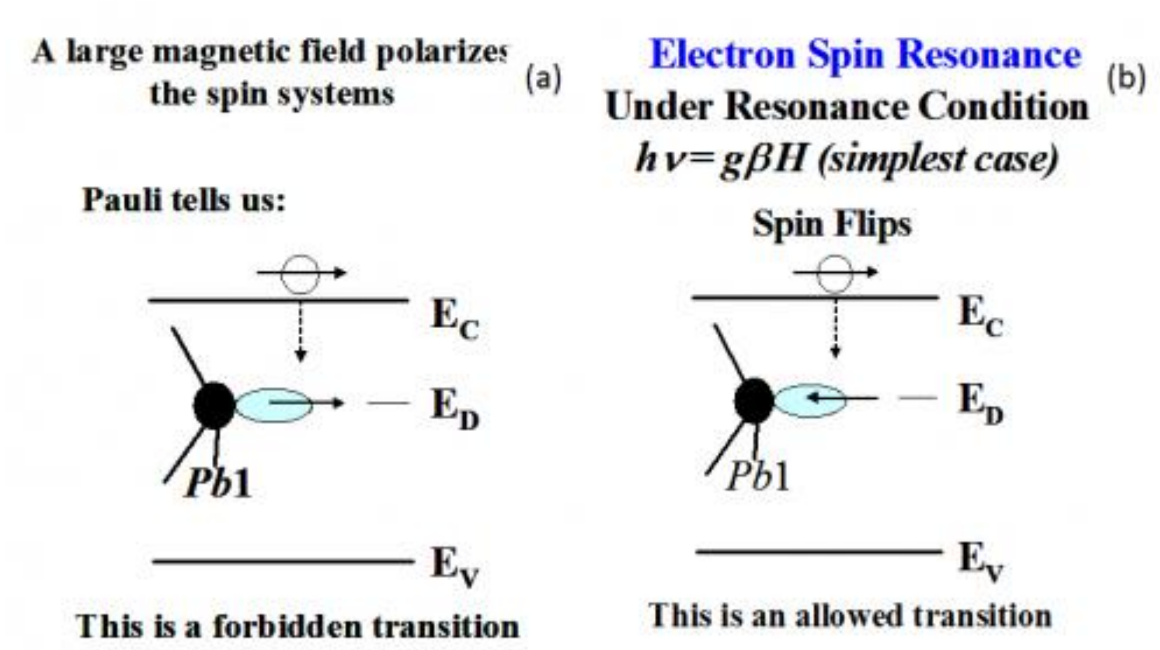

Figure 2: The Shockley Reed Hall Model with a large external field present [4]

This difference in measurement properties gives EDMR a few benefits over generic ESR. The first is that EDMR is 10^6 times more sensitive than ESR, which is especially important as electronic devices continue to get smaller and smaller and feature fewer defects as the processes to create these devices improve as well. EDMR also has the benefit of only measuring in electrically active regions as the microwaves in ESR might be absorbed by areas where electron transport doesn't occur in the device, allowing EDMR to observe the physical distribution of defects as well [7].

2.2.2) Specific EDMR Types

Most EDMR measurements are taken at high frequencies and fields, in the 1-10 GHz range. However there are a few more types of magnetic spectroscopy that can be done at much lower fields. These techniques are Low Field EDMR, which occurs at a few 100 MHz, and Zero Field EDMR, which has zero oscillating magnetic field. The Spin-Dicke effect that I will be studying in my research is actually form of EDMR that could be called Ultra-Low Field EDMR, operating at only a 1-10 MHz corresponding to 1-5 Gauss. The Spin-Dicke effect will potentially allow us to learn more about these new resonance techniques and potentially more about magnetoresistance in general. Due to the fact that only extremely low fields need to be accessed in order to create resonance, it could be a much cheaper alternative to operating at High field EDMR and maybe even cheaper than Low Field EDMR in some cases [8].

Since we are operating at extremely low frequencies, its important to have an understanding of Zero-Field EDMR. When the external magnetic field switches from negative to positive or vice versa, a large change in current is observed. This is called the Zero-Field effect. When the magnetic field is zero, all electron states will have similar energy, allowing the singlet and triplet states to mix at this point. This means that all states are accessible regardless of the radiation being applied. This Zero-Field carries some information about the material under scrutiny, but doesn’t have all of the information carried in other EDMR measurements. However, as a resonator isn’t needed to preform experiments and high magnetic fields don’t need to be achieved, Zero-Field EDMR is the cheapest way to attain information about a sample. Not utilizing a resonator can also help ascertain measurements in devices that are covered in different types of materials or are embedded within a microelectronic system, which is especially important with the rise of 3D FET architecture [8]. Understanding this effect is as important as the Zero-Field effect is something that cannot be removed from any Low-Field EDMR experiment. Using Zero-Field EDMR measurements in order to resolve the Spin-Dicke response will be very important in understanding and observing the Spin-Dicke effect.

2.2.3) Spin-Dicke Effect

The Spin-Dicke effect is a special type of Ultra Low-Field EDMR that occurs when the magnitude of the oscillating field is equivalent to the magnitude of the external field. As discussed previously, when an oscillating field is able to flip a deep level state and overcome the Pauli Exclusion Principle blocking effect, one observes an increase and decrease in current. It has been hypothesized [9] and proven [10] in Organic LEDs that when the magnetic field is about equal to the external field, the increase or decrease proportional to B, and also features a decreasing change in current when the magnetic field continues to increase. This means that besides just mixing the existing quantum states, the oscillating field is actually introducing new quantum states, some of which are blocking states that will decrease the change in current [9]. Before the oscillating field reaches the strength of the external field, the electron hole pair will resonate in phase with each other, but each of these electron deep-level pairs will have a random phase compared with the driving field. When the oscillating field reaches a value similar to the external field, the spins begin to act in phase with each other and their coherence results in a change in conductivity. The spins then become phase locked and there will be a decrease in the magnetoresistance of the device. This can be seen in Figure 3 [10].

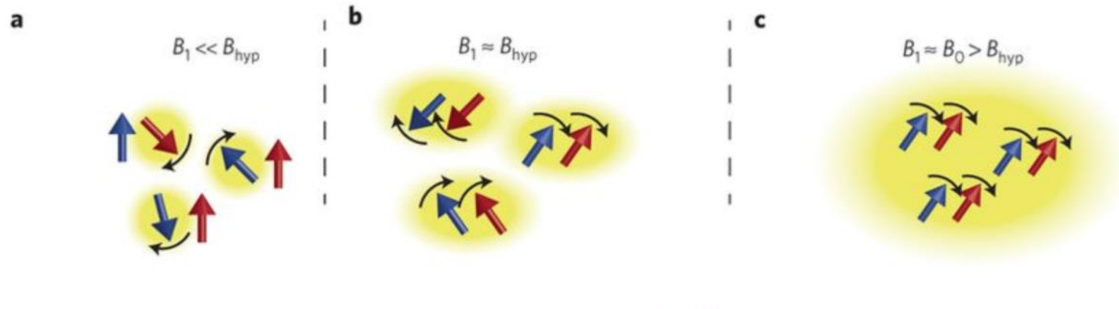

Figure 3: Electrons phases under the Spin-Dicke Effect [10]

It is important for these measurements to involve a stronger magnetic resonance value than the hyperfine fields due to nearby magnetic nuclei. These hyperfine fields must be overcome in order to have the electron and hole resonating in phase with each other during recombination [10]. My thesis will constitute experiments trying to detect these Spin-Dicke effects in inorganic devices such as SiC.

2.3) Resonance Physics

In order to produce the Spin Dicke effect in my SiC p-n junctions I needed to produce an oscillating magnetic field with a magnitude similar to the resonance magnetic field. I decided to produce this oscillation with a simple LC circuit with the magnetic field produced by the inductor. The resonance magnetic field would depend on a relation of the frequency of the coil, which is affected by the physical attributes of the solenoid as well as the capacitor used in the circuit. When simplifying these relationships the equation can be written as follows:

$$\nu = \frac{1}{2\pi\sqrt{LC}} = \frac{\sqrt{l}}{2\pi N\sqrt{uAC}} \quad (4)$$

where ν is the frequency, L is the inductance, C is the capacitance, l is the length, N is the number of coil turns, A is the coil area, and u is the permeability of free space. The magnetic field can also be related to the circuit parameters as follows:

$$B = Inu = \frac{VNu}{wLl} = \frac{V\sqrt{uC}}{\sqrt{Al}} \text{ (5)}$$

where B is the magnetic field of the coil, n is the turn density of the coil, I is the current, and V is the voltage. What is left is relating these two quantities with the resonance condition provided in the literature review:

$$\nu \approx 2.802 \left(\frac{MHz}{G}\right) B_{resonance} \text{ (6)}$$

where $B_{resonance}$ is the external magnetic field at which resonance occurs. We would like $B_{resonance}$ to be around the magnitude of the coil magnetic field that we can achieve with our coil parameters.

Chapter 3

Experimental

3.1) Coil Specifications

3.1.1) Coil Measurements

In order to get the oscillating magnetic field strength above the hyperfine strengths, we wanted the coil field to be as strong as possible. A lot of things that increase the magnetic field also cause the frequency to change as well. Obviously the area of the coil should be decreased as much as possible, but the measurement is limited since the sample must fit inside the coil. The sample and mount restricted the diameter to greater than 7.5 mm. Decreasing length and increasing capacitance have inverse effects on frequency and magnetic field amplitude. This is fine for fine-tuning the circuit but not for increasing the point where the resonance field matches the oscillating field. We could try decreasing the number of turns to increase frequency, and then change the capacitance to correct for the change, but this effect will still only see a small increase in frequency as the length is decreasing at the same rate, and the number of turns can only be decreased by so much and causes a little loss in stability of the magnetic field. I constructed many of these coils, most of which fell between the range of 1 MHz to 10 MHz. The final coil used had the following parameters: a length of 4 mm, an area of 33 mm^2, a capacitance of 2.3 nF, and 4 turns, to get an output of 1.2 Gauss at 12.1 MHz I used a function generator with a tunable output in order to create measurements of the effect of the resonator on the current when the magnetic field is increased through resonance.

3.1.2) Amplifier System

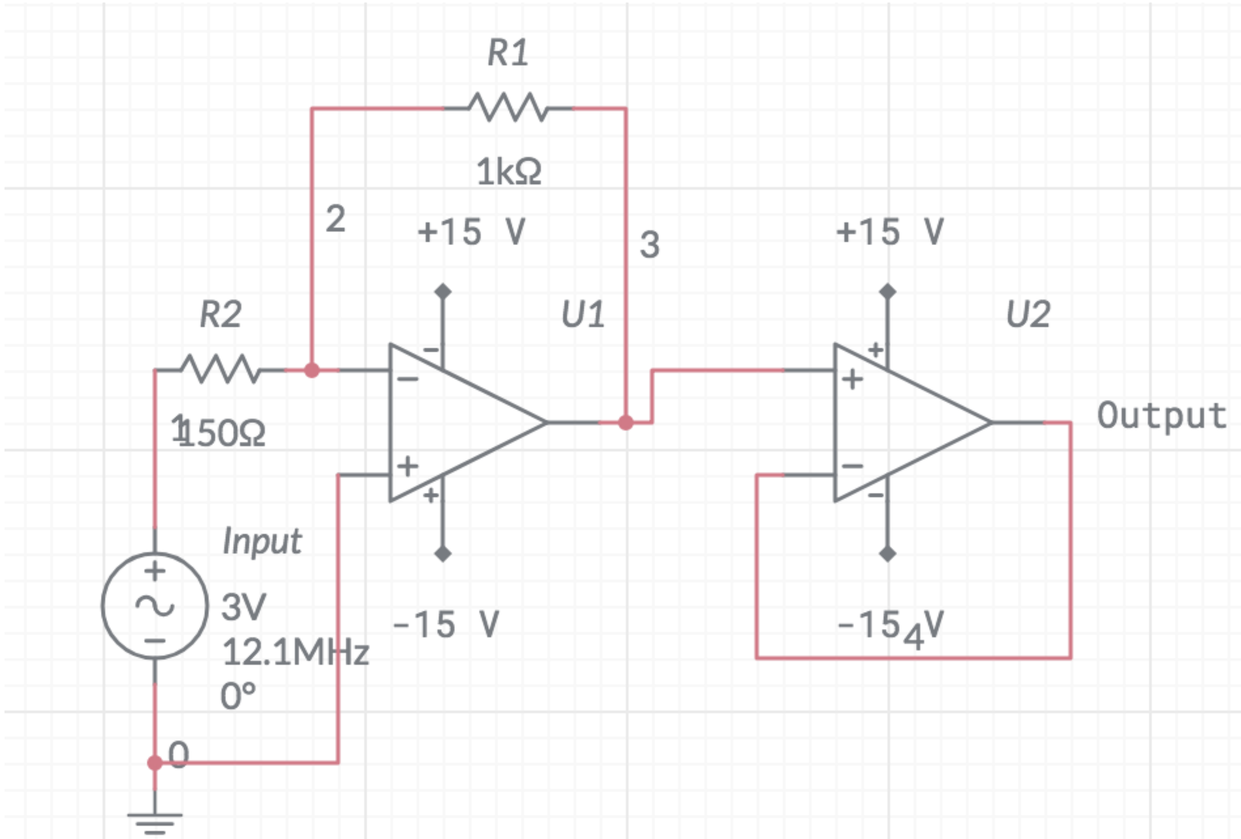

Figure 4: Amplifier System

I determined that the output of 1.2 Gauss would not be sufficiently above hyperfine interactions in order to generate the response I wanted. One variable that can obviously provide an increase is the voltage. Increasing the voltage has no effect on frequency but increases the oscillating magnetic field linearly. In order to create an amplification at 12.1 MHz, I decided to use a LM6172 operational amplifier and a BUF634 buffer in the shown in Figure 4. Using this setup allowed me to increase the magnetic field by a factor of 4. Using all of these parameters resulted in a magnetic field of around 5 Gauss at a frequency of 12.1 MHz; a 12.1 MHz frequency corresponds to a resonance field of 4.3 Gauss.

3.1.3) Compatibility with Spectrometer

After creating the coil, the next step was to create a frame so that the coil would be held stationary while the sample was placed within. The easiest way to make sure that this would be the case would be to create a 3D print of a casing that could be slipped into and held in place by the spectrometer. This casing would be designed with a specific coil in mind in order to create an exterior similar to the other coils but had internal dimensions to secure the coil. The end result is in Figure 5. These two pieces would then be glued together around the coil in order to make a box that can be placed into the spectrometer, shown in Figure 6. This frame allows the coil to be secured around the BNC port in order to take stress off of the wires while suspended, a hole that allows the sample to be inserted, and holes that will allow a sniffer coil to be inserted next to the device.

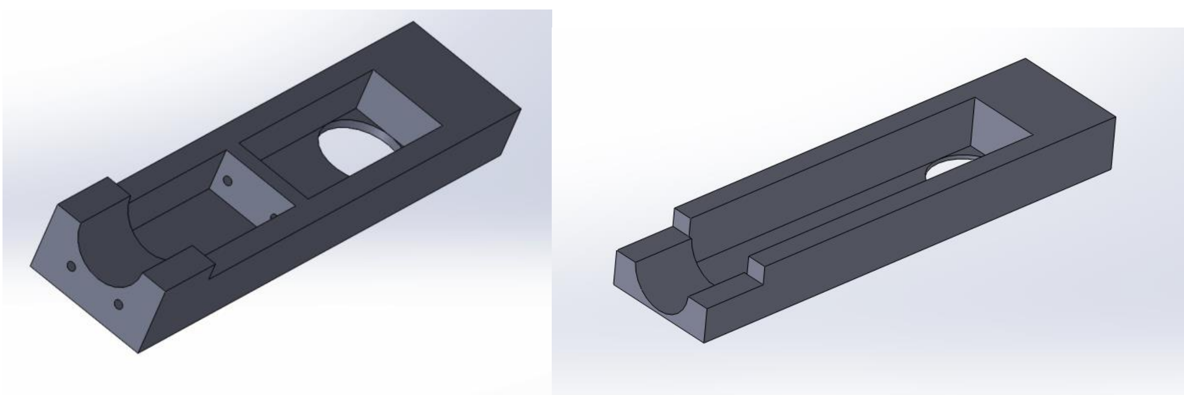

Figure 5: 3D Drawing of casing for coil

A sniffer coil is a single winding of coil that, when connected to an oscilloscope, measures a voltage that is proportional to the magnetic field to which it is exposed. This is extremely important to my experiments, as an accurate measurement of B_1 is needed in order to investigate the Spin-Dicke effect on these devices. By integrating the coil into my coil casing, I can make sure that the coil is aligned in a position to get the best reading of B_1 and also save time by not having to create another coil and reintroduce it to the system for every experiment.

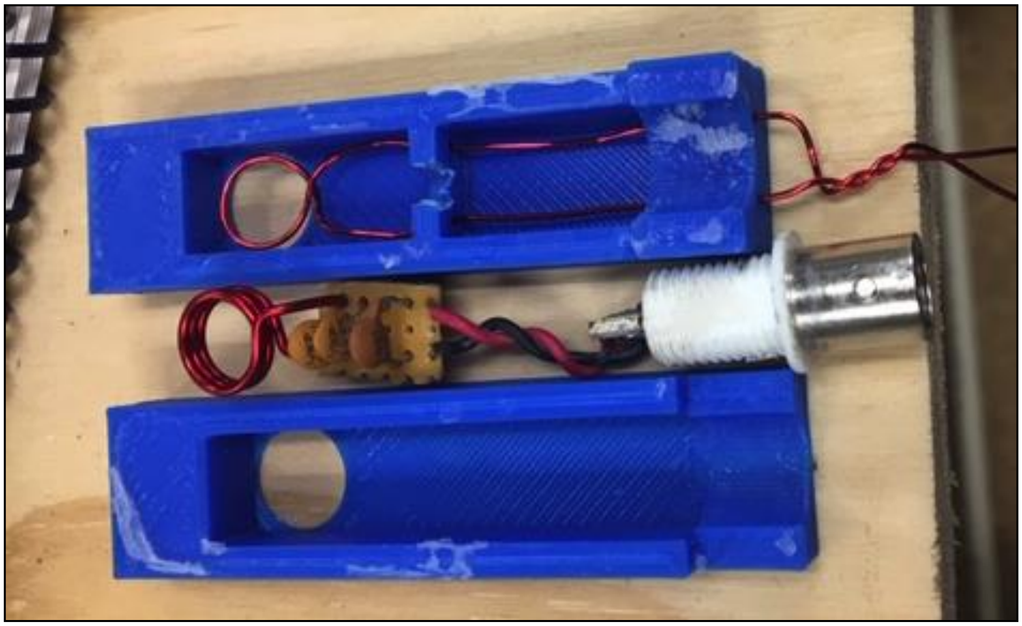

Figure 6: Casing for coil and coil

3.2) Spectrometer System

The spectroscopy system used for this experiment is shown in Figure 7. The spectrometer has the capabilities to ramp up the magnetic field while recording the current that is flowing through the device. This magnetic field is created using a series of Helmholtz coils. These coils produce a strong stable magnetic field. Inside these Helmholtz coils exist another, much smaller pair of Helmholtz coils. The smaller set of coils are known as the modulating coils. My experiments were done with a variety of modulation amplitudes and frequencies. The spectrometer is also housed in a system called the zero-Gauss chamber. This chamber's magnetic isolating layers eliminate the ambient magnetic field that is present outside the chamber.

Figure 7: Spectrometer system within Zero-Gauss Chamber

Chapter 4

Results and Discussion

4.1) Amorphous Boron Response

The first systems I used to test my experiment were amorphous boron films. The reason I used these films was to test the setup of my spectrometer to make sure the system worked. Amorphous boron is good for this as the zero-field response of this material is very large. That made it easy to tell if my device was giving me an actual signal or if there was just noise coming from the device. The zero-field from the amorphous boron can be viewed in Figure 8.

After getting this response, the next step was to test the response of the coil I constructed. I decided to use a 1.2 MHz coil, which corresponded to a resonance magnitude of 0.5 Gauss. I utilized a couple of magnitudes of B_1 to attempt to see the Spin-Dicke effect. Figure 8, shows that using a certain magnitude of magnetic field reduces the zero field effect. This reduction could be a form of the Spin-Dicke effect. However, the reason I chose the amorphous boron became an issue onto itself. Since the zero-field response was so large, it was impossible to resolve the resonance peaks caused by my coils. The zero-field continues much past the -10 and 10 Gauss on the figure, as the software will bring the maximum and minimum readings of each figure to zero, even if there is more zero-field response beyond that point. Besides just overlapping the zero field, the coil's resonance peaks will also overlap one another. This meant that the frequency must be increased regardless of the sample used. I decided to pursue a material with a much smaller zero-field response, and one that would also have much more applicability in the world of semiconductors due to its wide use, SiC, as well as make another coil to increase the frequency.

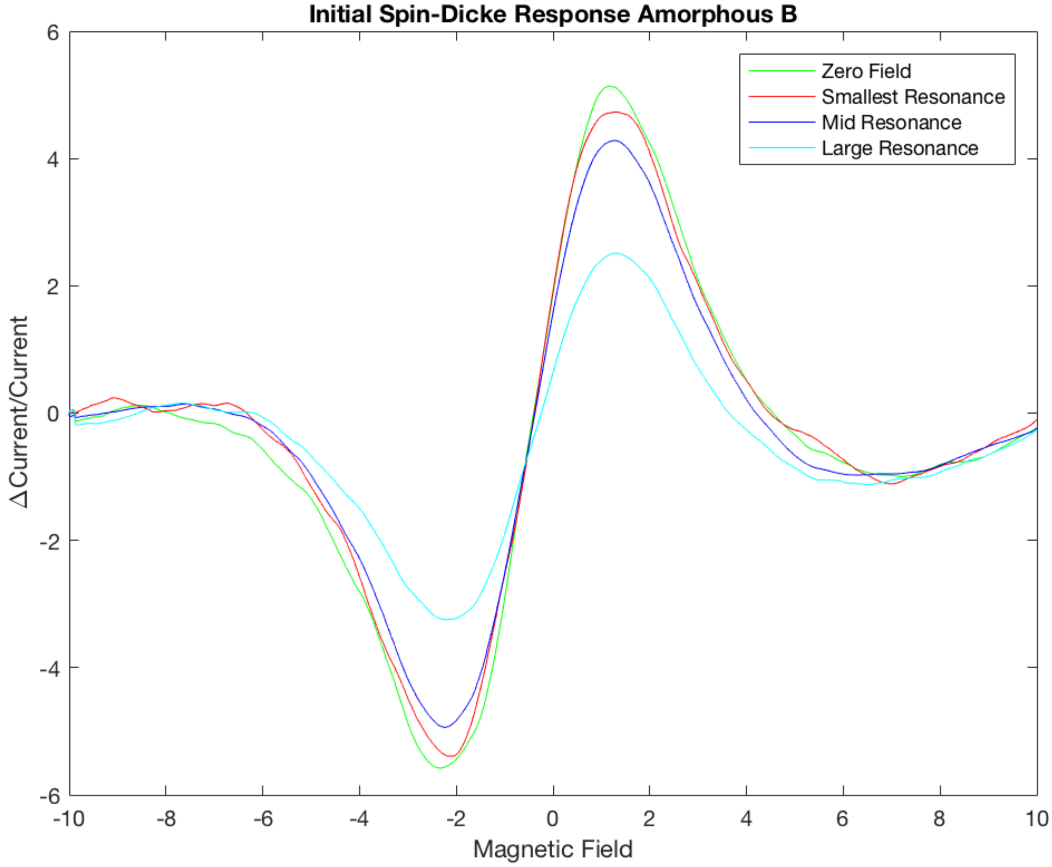

Figure 8: Amorphous Boron at several resonance magnetic fields at 1.2 MHz

4.2) Initial SiC Response

After constructing the higher frequency 12.1 MHz coil, I decided on testing on a device that will allow the response to be better resolved. The device I decided on was a SiC p-n junction. The devices that the Jet Propulsion Lab will be using for deep space applications would be made from SiC due to its robustness. The results of the scans are shown in Figure 9. However, the strength of my coil could only reach a magnitude of 1.2 Gauss. The frequency 12.1 MHz corresponds to a resonance of about 5 Gauss. This discrepancy in magnetic field means that I needed to increase the magnitude of my coil. In order to do this, I constructed the amplifier specified in the experimental section.

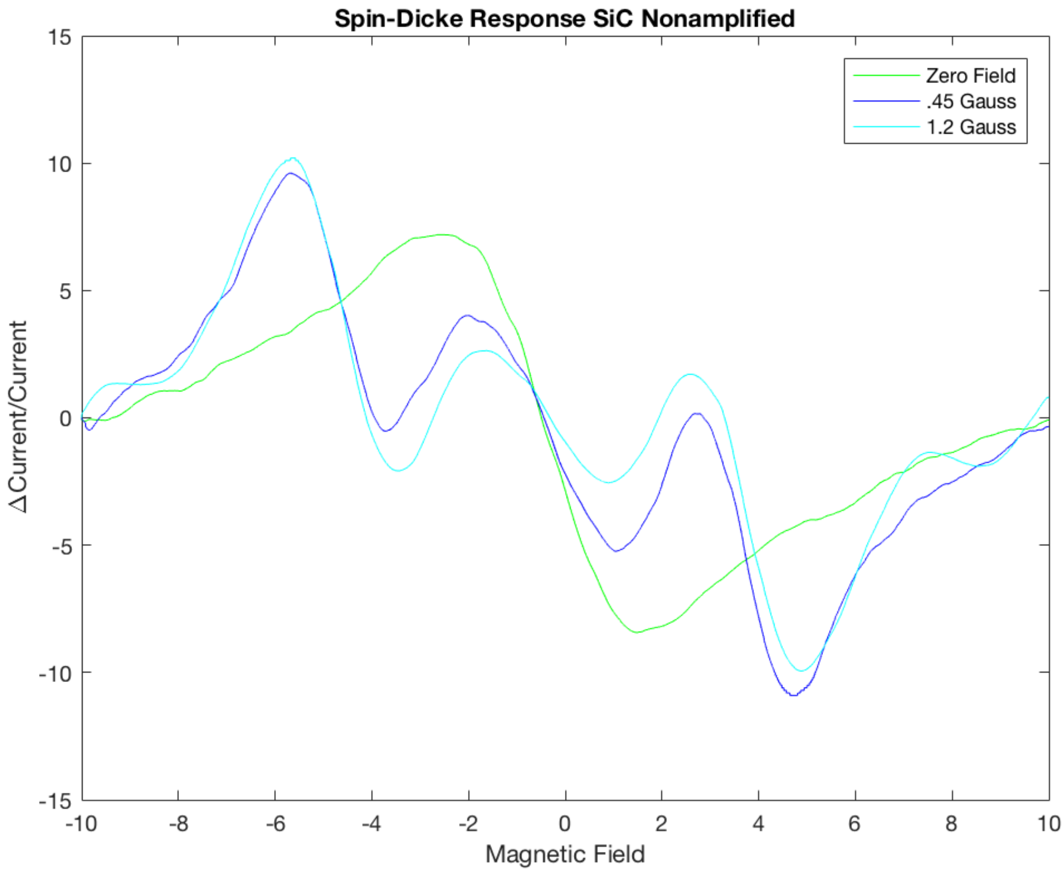

Figure 9: SiC resonance at 12.1 MHz without using the amplifier

4.3) Final SiC Response

Using my amplifier on my coil allowed the magnitude of the coil to be amplified by a factor of about 4, bringing my amplitude to about 5.1 Gauss. With this oscillating magnetic field strength the coil magnetic fields were much closer to the resonance field strength of my coil. Here magnetic field strength also exceeded the hyperfine conditions of SiC, having the next oscillating magnetic field be stronger than a large majority of the hyperfine interactions of SiC.

[11] The scans produced by this coil are shown in Figure 10. As one can see, the zero field effect still overlaps the resonance peaks, but they are definitely much further from the center of the signal and won't overlap each other. There is a definite shift in response when changing B_1 as well.

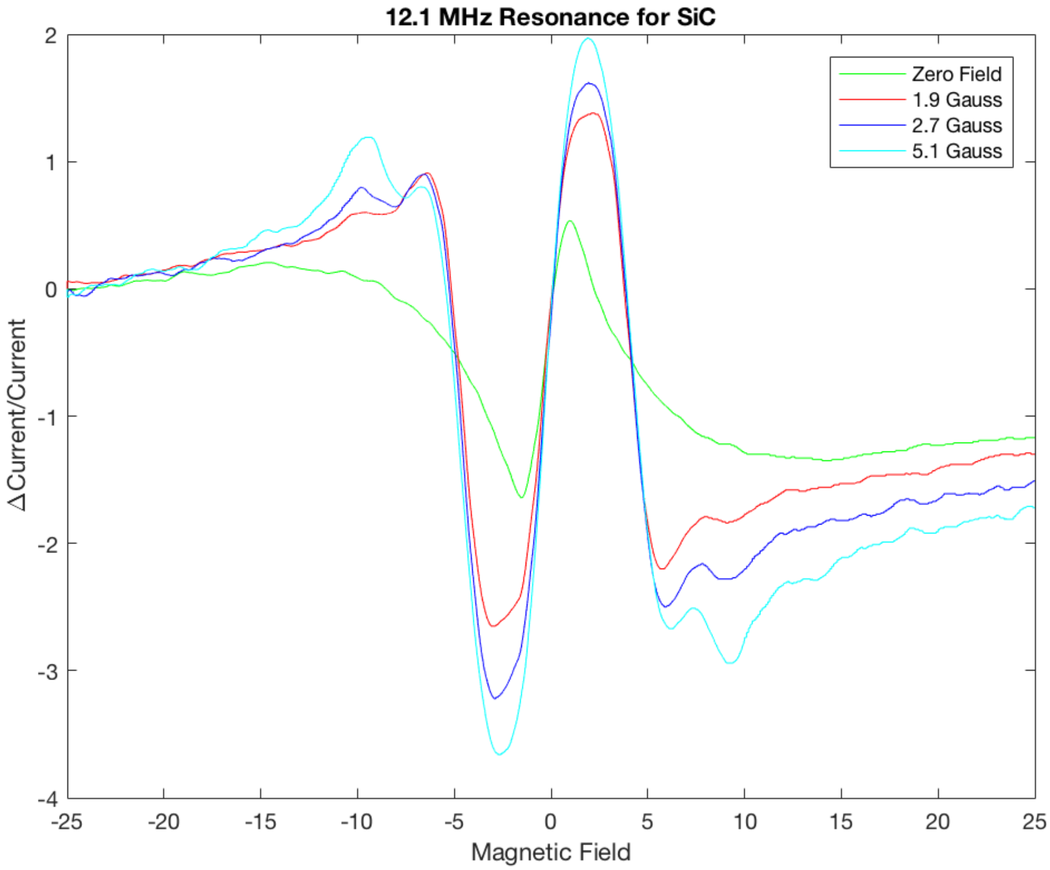

Figure 10: Resonance for SiC using an amplifier

Chapter 5

Conclusion

5.1) Conclusions

In conclusion, I was unable to get conclusive evidence of the Spin-Dicke effect while in the Spin-Dicke regime of oscillation. However, I laid a large sum of groundwork in order to for this effect to be seen in the future. Using my amplification system is a must for the system, as increasing voltage is incredibly important for these measurements. The coils that I produced became much closer and closer to exhibiting characteristics that would definitely land my coil above the hyperfine interactions of SiC and other materials. I also produced a few preliminary scans to show that this is the direction that we must travel in order to see the effect, and perhaps might even exhibit the effect if the response could be resolved from the zero field response.

5.2) Next Steps

There are a few directions that can be taken from this position. I think the most important of which is figuring out a way to resolve the signal from the zero field. The effect seems to either diminish or strengthen the zero field as well as introducing the resonance peaks that we see on the scans, so purely subtracting off the zero field is not enough to resolve the signal. If there was a way to separate the signal, or to scale up the zero field response before subtracting it off, I think that the Spin-Dicke effect would be a lot easier to measure and even be quantified. Another option is to look for another material with a smaller zero field. I think this is unlikely however, as SiC was the material that I was most interested in, and getting a system that would work for more materials rather than just one or two would allow a better understanding of this effect on inorganic semiconductors as a whole.

One other thing that can be done is by creating other coils with a larger frequency. I think that this is the best way to proceed, but was the hardest for me to do. I tried producing other coils after the 12.1 MHz coil, but couldn’t make anything larger than the 12.1 MHz frequency. I finalized a coil that was around 8 MHz, and would love to do scans that utilize this coil but I know that similar issues with the 12.1 MHz coil will still emerge. One idea that I think would work would be using smaller samples. The devices that I was using are extremely small, on the scale of micrometers. The reason that the area was as large as it was is that the current method for obtaining samples is using a diamond scribe, which cuts out a chunk of the SiC wafer to be put on a sample holder. By using smaller sample holders and much smaller samples, the area of the coil can be vastly decreased, increasing the magnitude and frequency of the response. This would require a new method of preparing samples however, but would be useful in looking at this strange phenomenon.

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Education

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- Designed, 3D printed, and wired a Helmholtz Coil for a spectrometer that studies defects of semiconductor devices using magnetic resonance techniques around zero-field during the summer of 2017
- Conceived and built LC circuits and an amplifier that operate at radio frequencies and produce a strong magnetic field in the coil of a few miliTesla to observe unique spin interactions in materials during the summer of 2018
- Plan and perform experiments using magnetic resonance to analyze magnetoresistance, hyperfine interactions, and the spin interactions caused by these coils

Carter Mechanical, Intern — **Summers 2015/2016**

- Estimated cost of jobs by reading blueprints to provide a price to bid for construction rights
- Managed documentation of spending and looked for discrepancies in accounting

Extracurricular Activities

Engineering Ambassadors, Ambassador — **Fall 2017- Present**

- Present to middle and high school students across Pennsylvania to get students excited about engineering careers
- Facilitate on campus activities, including engineering based tours for prospective students
- Received training in public speaking and making technical talks seem non-technical for a younger audience

Men’s Ultimate Frisbee, Vice President (2016-17), Captain (2017-present) — **Fall 2015-Present**

- Fundraised over $4,000 during one semester for Penn State’s A-team
- Plan out practices and refocus the team atmosphere to enhance the team’s performance
- Coordinate travel and hosting logistics for tournaments and community service events for the team

International Experience

Mechanical Engineering Product Design Programme, Student — **Summer 2016**

- Worked in highly interdisciplinary teams with students pursuing assorted majors and hailing from The Pennsylvania State University, Brigham Young University, and the National University of Singapore
- Designed and built a compressing dustpan as an economically and environmentally sustainable solution to a problem our team identified in Singapore
- Utilized design processes that focused on iteration and face-to-face Singaporean consumer interaction

Skills and Awards

Skills

- Proficient in MatLab, C++, Java, Mathematica, LaTeX, Multisim, and Microsoft Office
- Proficient in 3D printing and design through Inventor and SolidWorks

Awards

- Erickson Discovery Grant — **Summer 2018**
- Bert Elsbach Honors Scholarship in Physics — **Fall 2017**
- Academic Excellence Scholarship — **Fall 2015-Present**
- Dean’s List — **All Semesters**