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TECHNICAL REPORT

A New Approach to Develop Atomic Scale Understanding of Radiation Effects in Emerging Nanoscale Memory and Logic Materials and Devices

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Executive Summary

We have utilized several electrically detected magnetic resonance (EDMR) techniques to develop an atomic scale understanding of radiation damage (and other) related reliability problems in several systems of great importance in emerging memory and logic devices. Systems and materials involved in the study include tri-gate (also called FinFET) metal oxide silicon field effect transistors (MOSFETs), low dielectric constant, so-called low -k dielectrics, utilized in interlayer dielectrics of present-day high performance integrated circuitry, SiGe MOSFETs, and HfO₂ resistive random-access memories.

In this study we have utilized relatively novel techniques: comparisons of high and low frequency and field EDMR measurements and EDMR utilizing spin dependent recombination and spin dependent trap assisted tunneling. Our work has resulted in a considerable advance in the understanding of the atomic scale mechanisms of radiation damage on an atomic scale in FinFETs, low-k interlayer dielectrics, and more modest progress in the understanding of radiation damage and electrically active defects in HfO₂ resistive random-access memories and SiGe MOSFETs.

Very briefly, our most significant findings are as follows:

(1) We find that the radiation induced defects in Tri-Gate (also called FinFET) devices are quite similar but not likely perfectly identical to the silicon dangling bond defects (P_b centers) found in irradiated planar silicon/ silicon dioxide devices.

(2) We find that radiation damage involves major changes in the chemical structure of the defects involved in radiation damage of SiOC:H low -k interlayer dielectrics. The EDMR results show, reasonably definitively, that the defects involved in the leakage currents are silicon and carbon dangling bonds. The results also indicate, with less certainty, that this transition in defect population with irradiation involves a switch from silicon to carbon dangling bonds with irradiation. It can be inferred from these results that multiple defect/hydrogen interactions are involved in radiation damage in these systems.

(3) We find that gamma irradiation creates or in some way alters defects involved in the electronic transport which occurs in HfO₂ based resistive random access memory devices. Although we clearly observe the generation of a radiation induce EDMR response in measurements of RRAM current, the observations do not allow us to identify the defects responsible with absolute certainty. However, the results are consistent with O₂⁻ centers.

(4) We find that in SiGe MOSFETs, semiconductor/ dielectric interface traps generated by gamma irradiation as well as interface traps existing prior to irradiation are clearly not dominated by silicon dangling bonds but are probably dominated by germanium dangling bonds or some other defect in which germanium atoms play an important role.

(5) In addition to the study's contribution to the atomic scale mechanisms of radiation damage in the systems under study, we believe our work involves two other significant contributions. First, much of our efforts have been devoted to the development of the hardware utilized in the EDMR studies. We did not invent low field EDMR but we have made a number of modest innovations in our home built EDMR spectrometers which have made them more practical for device physics studies. Secondly, we believe that our work may serve as a sort of road map for future studies of radiation effects utilizing advanced magnetic resonance techniques. The most significant aspect of this contribution is the demonstration of the utility of multi-frequency EDMR in which very high (9.5GHz) and very low (85 to 500MHz) frequency results on the same devices are compared. We were not the first to point out the fact that EDMR detection has a near frequency independent sensitivity. We were also not the first to note that multi-frequency magnetic resonance can provide insight into defect structure. However, we believe the results of this study provides a strong argument for the widespread applicability of such measurements in solid state device physics.

Individuals involved in the study:

PI, Patrick M. Lenahan

Graduate Students:

Ryan J. Waskiewicz

Colin McKay

Duane J. McCrory

Stephen J. Moxim

Kenneth Myers

Ashton Purcell

Fedor Sharov

Seven students have been supported in part by this project. In no case have any students been supported entirely by the project. One Ph.D. thesis has resulted as a result of very substantial support from this project, that of Colin McKay. The thesis has been included as an appendix at the end of this report. It will eventually be available on-line; however, the thesis defense took place in late February, 2021 and it is as yet otherwise available. Duane McCrory's Ph.D. thesis work was, in part, supported by this grant. McCrory's thesis is available online [1]. Five other students, still in graduate school have been supported in some part by this grant.

Publications Resulting from The Study:

(partial support) N.J. Harmon, Stephen R. McMillan, James P. Ashton, Patrick M. Lenahan, Michael E. Flatte,” Modeling of Zero-Field Magnetoresistance and Electrically Detected Magnetic Resonance in Irradiated Si/SiO₂,” IEEE Transactions on Nuclear Science, vol.67, no.7, 1669-1673 (2020)

(partial support) Stephen J. Moxim, James P. Ashton, Patrick M. Lenahan, Michael E. Flatte, Nicholas J. Harmon, and Sean W. King, “Observation of Radiation Induced Leakage Current Defects in MOS Oxides with Multi-Frequency Electrically Detected Magnetic Resonance and Near Zero Field Magnetic Resonance, IEEE Transactions on Nuclear Science, vo.67, no.1, 228-233 (2020)

Kenneth J. Myers, Patrick M. Lenahan, Brad C. Bittel, and Inanc Meric “Exploring Negative Bias Temperature Instability in Tri-Gate MOSFETs Through Electrically Detected Magnetic Resonance, 2019 IEEE International Integrated Reliability Workshop,” Stanford University Sierra Camp, California, October 2019 Conference Proceedings, called The Final report, pages 114-117 (2019)

K.J. Myers, R.J. Waskiewicz, P.M. Lenahan, C.D. Young,” A Multi-Field and Frequency Electrically Detected Magnetic Resonance Study of Atomic Scale Defects in Gamma Irradiated Modern MOS Integrated Circuitry,” IEEE Transactions on Nuclear Science, vol.66, no. 1, 405-412 (2019)

D.J. McCrory, P.M. Lenahan D.M. Nminabapiel, D. Veksler, J.T. Ryan, and J.J. Campbell, “Total Ionizing Dose Effects on TiN/Ti/HfO₂/TiN Resistive Random-Access Memory Studied Via Electrically Detected Magnetic Resonance, IEEE Transactions on Nuclear Science, vol.65, no.5, 1101-1107 (2018)

Reference:

[1] McCrory, D. (2019). Magnetic Resonance in a Wafer Probing Station. PhD Dissertation
https://etda.libraries.psu.edu/files/final_submissions/19408.

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INTRODUCTION

We have utilized several electrically detected magnetic resonance (EDMR) techniques to develop an atomic scale understanding of radiation damage (and other) related reliability problems in several systems of great importance in emerging memory and logic devices. Systems and materials involved in the study include tri-gate (also called FinFET) metal oxide silicon field effect transistors (MOSFETs), low dielectric constant, so-called low -k dielectrics, utilized in interlayer dielectrics of present-day high performance integrated circuitry, SiGe MOSFETs, and HfO₂ resistive random-access memories. Unsuccessful attempts were made to explore other systems with EDMR, most notably GaN devices. Since no useful information came out of these unsuccessful studies no further mention is made of the work in this report. To make this report comprehensible to a fairly wide audience, the first topic covered is the study's primary technique, EDMR.

I. Experimental Equipment, Set Up and Procedures

1a. Background: Electrically Detected Magnetic Resonance

Electrically detected magnetic resonance [1-3] is an exceptionally sensitive electron paramagnetic resonance (EPR) [4-6] detection technique. EPR techniques have unparalleled analytical power to identify the physical and chemical nature of point defects, such as the trapping centers which limit the performance of solid- state electronic devices. Conventional EPR has several fundamental shortcomings which seriously limits its applications in investigations of nanoscale devices. Three shortcomings are most important. (1) Classical EPR detection has a sensitivity of roughly ten billion total defects within the sample under study. Essentially no nanoscale devices have that many defects. (2) Classical EPR is sensitive to all the paramagnetic defects within the sample under investigation. This is a problem. Suppose one wishes to study performance limiting defects in a MOSFET. The thickness of the semiconductor substrate upon which the device resides is inevitably many orders of magnitude thicker than the active layer of the device, making it possible that the EPR response of the defects in question may be overwhelmed by technologically irrelevant defects far below the active region of the device. (3) Classical EPR sensitivity is quite strongly field and frequency dependent, with measurements much below about 9 GHz and a field of about

0.3 Tesla relatively insensitive. This can make the analysis of complex “messy” spectra likely to be observed in new and emerging materials and systems quite difficult.

EDMR overcomes these problems, providing a sensitivity typically about seven orders of magnitude superior to that of conventional EPR. EDMR is also exclusively sensitive to defects which are within the active area of the device under study and it is exclusively sensitive to those defects which influence device performances. In addition, the sensitivity of EDMR measurements is very nearly field and frequency independent. This field/ frequency independent sensitivity allows for the possible deconvolution of some complex and messy spectra by separating out the two physical phenomena which most commonly determine the spectral parameters, spin orbit coupling and electron nuclear hyperfine interactions. The two most sensitive EDMR techniques are EDMR via spin dependent recombination (SDR EDMR) and EDMR via spin dependent trap assisted tunneling (SDTAT EDMR). We have utilized both techniques in our study. To make this report comprehensible to a reasonably wide audience, a brief explanation, first of EPR in general and then of the two EDMR techniques is provided.

I b. Introduction to the Interpretation of Magnetic Resonance Spectra

Electrically detected magnetic resonance [1-3] is based on electron paramagnetic resonance (EPR) [4-6]. To understand the results presented, we provide a brief discussion of EPR. Consider a sample containing point defects with unpaired electron spins which is placed in a microwave cavity within an electromagnet. Consider the simplest of cases when the electron is unaffected by its surroundings. When a large magnetic field B_0 is applied, the energy of electrons within these defects will be split into two levels. These levels are determined by the electron's spin quantum number, m_s , which can have a value of $+1/2$ and $-1/2$. The sample is also subjected to a microwave field of magnitude B_1 . In the simple case of an unpaired electron otherwise unaffected by its surroundings, when the microwave frequency ν times Planck's constant h is equal to the electron energy splitting (Zeeman splitting) $\Delta E = g_e \mu_B B_0$, the sample will absorb microwaves and the unpaired electron spins will "flip" spin. Here, g_e is the Landé g factor ($g_e \approx 2.0023$) and μ_B is the Bohr magneton. At resonance, the electron transitions from its $+1/2$ to $-1/2$ spin state (or vice versa). For the simple case of an electron unperturbed by its local environment, the resonance condition is given by:

$$h\nu = g_e \mu_B B_0 \quad (1)$$

Perturbations to the resonance condition (1) provide structural information about the defects under study. Two of the most important perturbations are spin-orbit coupling and electron-nuclear hyperfine interactions. Spin-orbit coupling changes the Landé g factor g_e to an orientation dependent number often expressed as a second-rank tensor $\mathbf{g}$. Electron nuclear hyperfine interactions are caused by the interaction between the magnetic moment of the electrons and nearby magnetic nuclei. These two interactions can be described via a spin Hamiltonian of the form:

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_i \mathbf{I}_i \cdot \mathbf{A}_i \cdot \mathbf{S} \quad (2)$$

Here, $\mathbf{B}$ is the applied magnetic field vector, $\mathbf{g}$ is a second-rank tensor whose parameters depend on the spin-orbit coupling interactions, $\mathbf{S}$ is the electron spin angular momentum operator, $\mathbf{I}_i$ is the nuclear spin angular momentum operator for the i^{th} nucleus, and $\mathbf{A}_i$ is the hyperfine coupling tensor for the i^{th} nucleus.

The values and distribution of $\mathbf{g}$ tensor components depend on spin-orbit coupling and defect energy levels. It is thus often possible to glean physical and chemical information about defects from this information. Although the information is not without ambiguity, it is generally quite helpful. A standard perturbation theory calculation relates the $\mathbf{g}$ tensor components to defect physics as follows for dangling bond defects in particular [4-6]:

$$g_{ij} = g_e + \Delta g_{ij}, \quad (3)$$

where

$$\Delta g_{ij} = -2\lambda \times \sum_{ij} \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0} \quad (4)$$

Here, g_e is the free electron $\mathbf{g}$ value, and Δg_{ij} is the deviation of the respective tensor component from g_e . The atomic spin-orbit coupling constant is λ , and i and j correspond to the principal axes directions. Since λ depends on the charge in the nucleus and the electron wave function, chemical and physical information may be obtained from the measurement. Unfortunately, the denominator terms ($E_n - E_0$) come from energy level difference with respect to the observed paramagnetic state energy. Therefore, there are limits to what conclusions may be drawn from this measurement. One may however clearly conclude that a significant change in $\Delta \mathbf{g}$ means a significant change in defect structure. Also, the atomic spin-orbit coupling constants are strongly dependent upon nuclear charge; the greater the nuclear charge the larger the constant. Thus, when trying to distinguish between a carbon dangling bond and a silicon dangling bond or a silicon dangling bond and a germanium dangling bond, these expressions are quite useful.

The effects of hyperfine interactions are also often quite useful in elucidating defect structure. In effect, the hyperfine interactions are a measure of the magnetic field of nearby nuclei averaged over electron wave functions. No two nuclei have identical nuclear moments; many elements have multiple naturally occurring nuclei. Because of these features, the hyperfine contributions to EPR spectra can often provide absolutely definitive information about defect chemistry and structure. Other perturbations exist and are peripherally relevant to this study, such as electron-electron dipolar and exchange interactions.

Conventional EPR has a sensitivity which scales with the field and frequency of the measurement. Hyperfine interactions have a roughly field independent effect on resonance spectra, whereas the effects of $\mathbf{g}$ are essentially proportional to the field. Thus, resonance measurements at very different fields can be immensely useful. Since conventional EPR measurement sensitivity

depends upon the polarization of the spin system, ultra-low field measurements with conventional EPR have extremely low sensitivity [4-6]. EDMR overcomes these limitations. It has a near field and frequency independent sensitivity and is only sensitive to electrically active defects. EDMR thus offers great advantage in the analysis of resonance spectra.

I c. Spin Dependent Recombination

One transport mechanism detected through EDMR is spin dependent recombination (SDR). SDR can be understood through seminal work of Kaplan, Solomon, and Mott and subsequent work refining their ideas [1-3]. The following provides a simplified discussion of SDR. Consider a conduction electron which encounters an unpaired electron spin residing at a deep level defect. The conduction electron and trapped electron will couple to form an intermediate spin state. These spin states can either be singlet states ($S = 0$) with basis state $S_0 = \frac{(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)}{\sqrt{2}}$ with $m_s = 0$ or triplet states ($S = 1$) with basis states $T_+ = |\uparrow\uparrow\rangle$, $T_0 = \frac{(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)}{\sqrt{2}}$, and $T_- = |\downarrow\downarrow\rangle$ with $m_s = +1, 0$, and -1 respectively.

The conduction electron transition to the deep level will be forbidden by the Pauli Exclusion Principle if both electrons have the same spin quantum number. These triplet states will tend to dissociate and there will be no subsequent electron-hole recombination. (Recombination via triplet states could not conserve spin angular momentum since $S = 1$). However, under resonance, spin flipping events will transform triplet states into singlet states. Now the conduction electron and the electron residing at the deep level defect have anti-parallel spins. This is now an allowed transition and the conduction electron will fall into the deep level defect and subsequently recombine with a valance band hole (recombination via singlet states does conserve spin angular momentum since $S = 0$). In SDR, the flipping of the trap center spins is generally observed through a change in recombination current. This process is illustrated in Fig. 1.

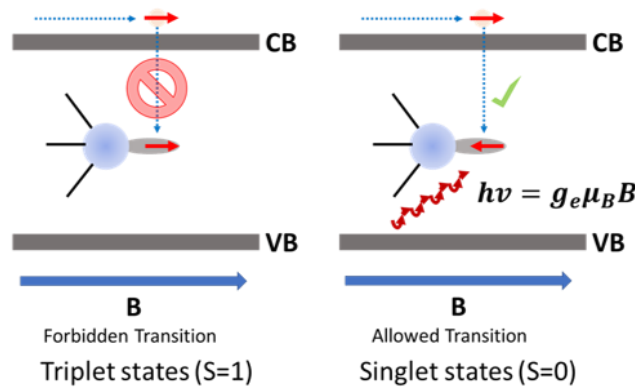


Figure 1. Illustration of SDR: (left) triplet state dissociation and (right) singlet state

In the SDR/ EDMR measurements, the device current is monitored while simultaneously exposing the device under observation to microwave or radio frequency irradiation and a large slowly varying magnetic field. When the EPR resonance condition is satisfied, recombination increases

and the current changes. A plot of the change in current versus field is almost the same in shape as the conventional EPR spectrum of the observed defect; however, the sensitivity of the measurement is much greater, typically by about a factor of ten million better. A limitation of the simple SDR EDMR measurement is the range of the bandgap which it probes. Because it includes charge carrier recombination through deep level defects, [7, 8] SDR is sensitive to levels near the middle of the bandgap and is not sensitive to levels near the band edges. This is not necessarily a serious limitation for studies of bipolar junction diodes and transistors in which near mid-gap levels are the primary concern. However, in studies of MOSFET radiation damage and other reliability problems, this is a big problem because defects with levels far from the middle of the gap can be seriously degrade device performance. This limitation can be overcome via spin dependent charge pumping (SDCP) [9,10].

SDCP is based on the classical electrical measurement of charge pumping [11]. In SDCP, a trapezoidal waveform is applied to the MOSFET gate, effectively moving the interface Fermi level through most of the interface band gap in which the charge pumping [11] measurement is combined with EPR. SDCP allows us to probe very nearly the entire bandgap. Usually, charge pumping measurements involve the grounding of MOSFET source and drain and the application of a trapezoidal wave form to the gate. This process is schematically illustrated in figure 2, for an n-channel transistor. The high voltage drives the interface Fermi energy to and very slightly beyond the threshold voltage, filling most of the interface traps with electrons. The low voltage drives the interface back to and slightly beyond accumulation, Holes flood the interface and are captured at the interface traps, thereby emptying out the interface traps in nearly all the band gap. The charge pumping process thus allows the EDMR measurement to access nearly all the semiconductor / dielectric bandgap, typically more than 80% on the band gap at the interface.

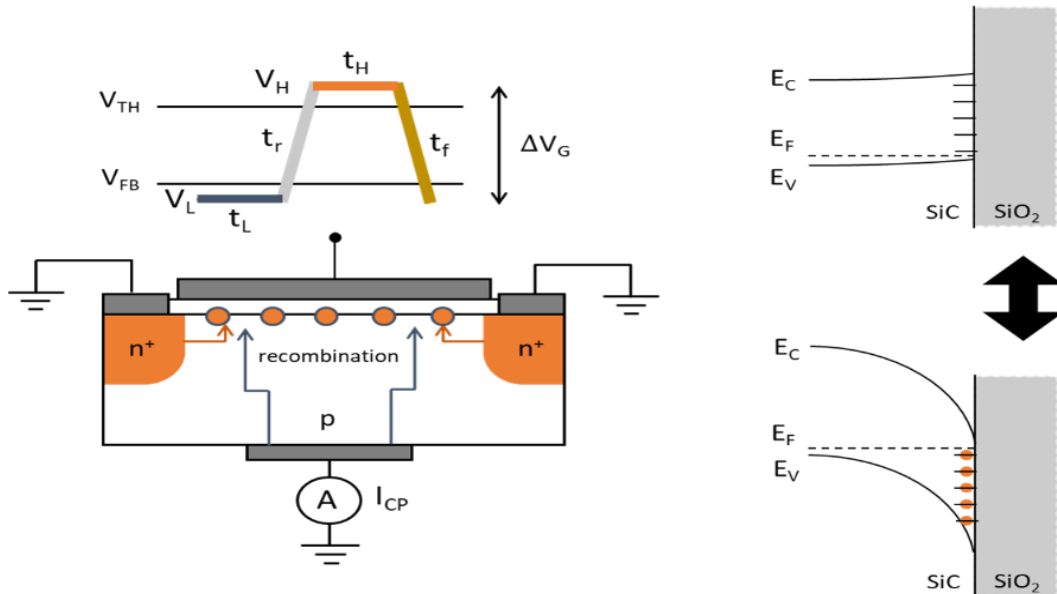


Figure 2. A schematic illustration of the MOS charge pumping (CP) measurement in which a trapezoidal waveform applied to the gate alternately fills and empties the interface traps. With the addition of radio frequency or microwave irradiation and a large slowly varying magnetic field, spin dependent charge pumping (SDCP) becomes possible. SDCP, like the simpler SDR EDMR measurement has a sensitivity about ten million times that of

conventional EPR.

A modest alteration in the scheme of Fig. 2 is required when SDCP measurements are made on silicon on insulator (SOI) FinFET MOSFETs in which the transistor's silicon body is on a silicon dioxide base. In this case, the body contact can be a structure in which the drain is replaced by an ohmic contact; as shown in figure 3, this is a p+ region replacing the drain.

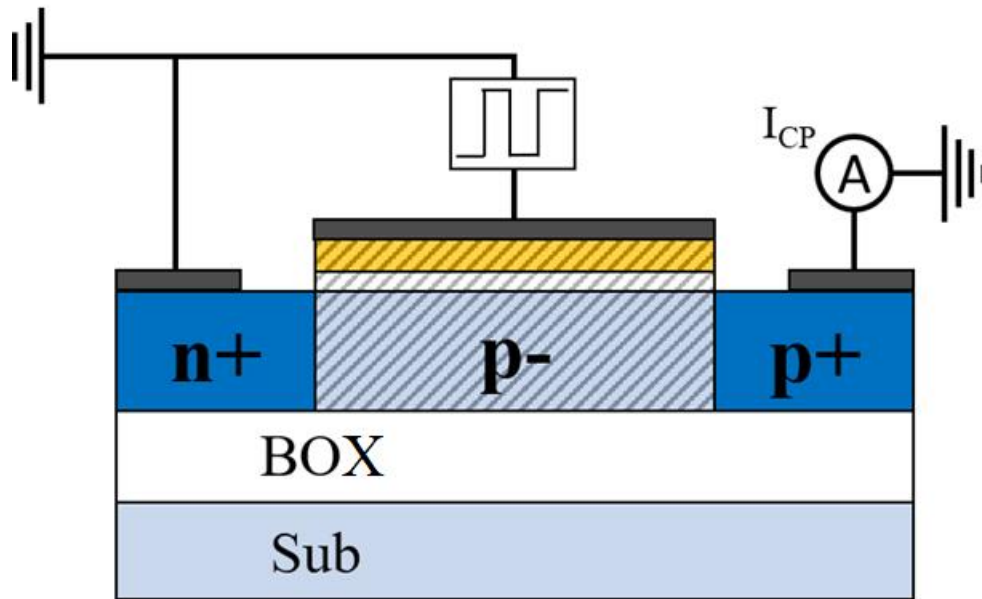


Figure 3. A schematic illustration of the MOS charge pumping (CP) measurement in which the transistor silicon is based on a dielectric layer. Here the CP current is measured through the p+ region which has replaced the drain. As in the illustration of figure 2, with the addition of radio frequency or microwave irradiation and a large slowly varying magnetic field, spin dependent charge pumping (SDCP) becomes possible.

I d. Spin Dependent Trap Assisted Tunneling

There is a second approach for EDMR which is useful for observing defects responsible for trap assisted tunneling in dielectrics. The most useful EDMR approach for the study of paramagnetic centers in thin dielectric films is spin dependent trap assisted tunneling (SDTAT) [12]. This process can be detected by monitoring leakage currents due to trap to trap tunneling which takes place in variable range hopping. As in spin dependent recombination, the process is easy to understand in a qualitative way in terms of the Pauli exclusion principle. The process schematically illustrated in Figure 4.

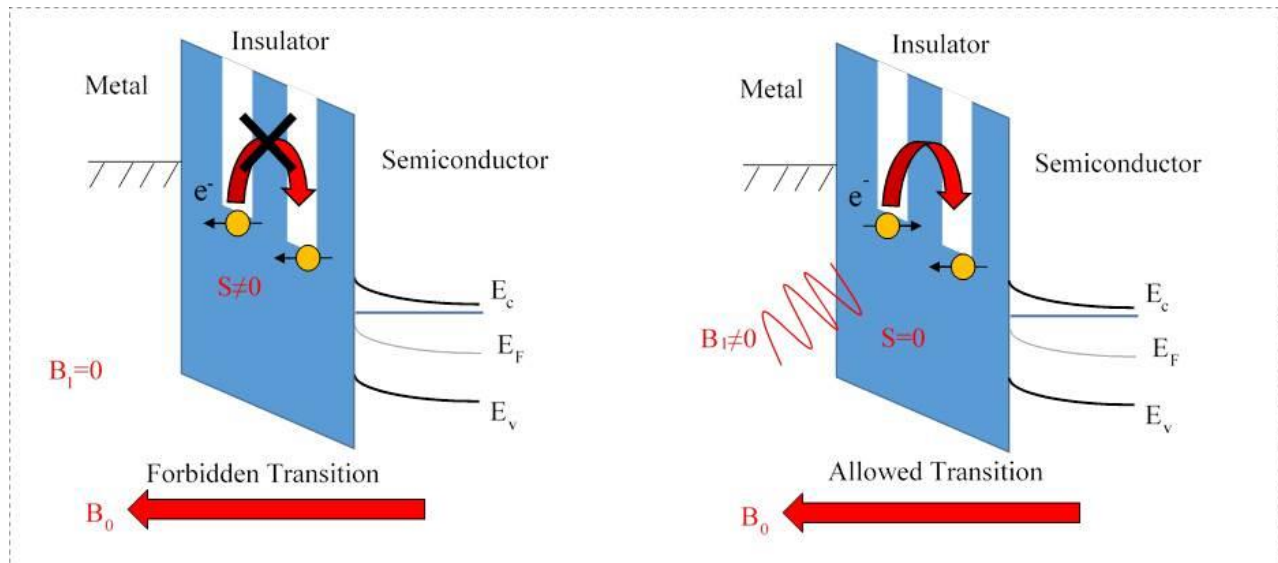


Figure 4. This figure illustrates spin dependent trap assisted tunneling in a dielectric

The cartoon illustrates the basic concept: tunneling between two paramagnetic defect sites is not possible if both possess unpaired electrons with the same spin quantum number. If, at resonance, one of the spins is “flipped” the formerly forbidden event becomes allowed and the current will change, thus generating a change in current which will, almost exactly, match up with the EPR spectrum. One can thus identify the chemical and physical nature of the defects involved in transport the tunneling current transport phenomena just as deep level centers in semiconductors can be identified via SDR. In this variant of EDMR, which we term spin dependent trap assisted tunneling (SDTAT) EDMR, the process is essentially analogous to SDR EDMR, except that, in this case one monitors the tunneling current as a function of a slowly varying magnetic field while simultaneously exposing the structure under study to radio frequency or microwave radiation (At least in principle, EDMR can also provide information about the separation of defects involved in transport.) The sensitivity of SDTAT EDMR is comparable to that of SDR EDMR.

I e. Multi -Frequency EDMR

One of the significant problems encountered in studies of new and emerging materials and devices is that, in terms of magnetic resonance spectroscopy, they are “messy.” That is, the geometries can be complex leading to EDMR spectra which can jumble several effects together. Examples of this “messy” spectroscopy occurs in FinFETs, low-k dielectrics, SiGe, transistors, and possibly in RRAM devices. Complex defect systems occur, for example in low dielectric constant, so called low-k films, used in state-of-the-art interlayer dielectrics. The degree of short-range order in such systems is inevitably very low. Thus, silicon dangling bond defects would have a range of local surroundings which would be far more variable than in the case of silicon dioxide. In silicon dioxide, virtually all the silicon dangling bond defects would involve three oxygen atoms back bonded to the central silicon with the dangling bond and, in most cases, the oxygens would be bonded to another silicon. This will not be the case in SiOC:H, where high concentrations of carbon and hydrogen atoms will inevitably result in differences in the immediate vicinity of these

defects. These differences will inevitably broaden the spectra and make it more difficult to deconvolute the two primary contributions to the shape of the spectrum: spin-orbit coupling and electron-nuclear hyperfine interactions. However, the field and frequency dependence of the two interactions are very different. The spin-orbit contributions effectively alter the spectra in a manner which scales with the measurement field and frequency. The hyperfine interactions provide a roughly field and frequency independent contribution. Thus, by comparing EDMR spectra taken with very different field and frequency combinations we can, to a significant extent deconvolute the two effects and through the deconvolution, learn a great deal of otherwise inaccessible information about defect structure and chemistry. The way in which this deconvolution process works can be understood in terms of a simple case: a dangling bond center which exhibits axial symmetry. In the simple case of an axially symmetric defect found in an amorphous system, the broadening due to spin-orbit coupling will correspond approximately to the difference in the g -values corresponding to the magnetic field parallel and perpendicular to the defect's symmetry axis: $g_{\parallel}$ and $g_{\perp}$, where we assign $B_{\parallel}$ and $B_{\perp}$ to their respective components:

$$B_{\parallel} \cong \frac{h\nu}{g_{\parallel}\mu_B}; \quad (5)$$

$$B_{\perp} \cong \frac{h\nu}{g_{\perp}\mu_B}. \quad (6)$$

From (2) and (3),

$$\Delta B \approx \frac{h}{\mu_B} \left| \frac{1}{g_{\perp}} - \frac{1}{g_{\parallel}} \right| \nu. \quad (7)$$

Making the approximation that $g_{\parallel} \approx g_{\perp} \approx 2$,

$$\Delta B \approx \frac{h}{\mu_B} \left| \frac{\Delta g}{4} \right| \nu \quad (8)$$

By solving (5) for Δg in terms of both the high and low field/frequency EDMR linewidths, ΔB_{high} and ΔB_{low} , we arrive at:

$$\Delta g \approx \frac{4\mu_B}{h} \left(\frac{\Delta B_{high} - \Delta B_{low}}{\nu_{high}} \right), \quad (9)$$

where ΔB_{high} and ΔB_{low} are the spectra's linewidths at high and low field, respectively, and μ_B and h have been previously defined in the discussion of expression (2). The process is schematically illustrated in Figure 5.

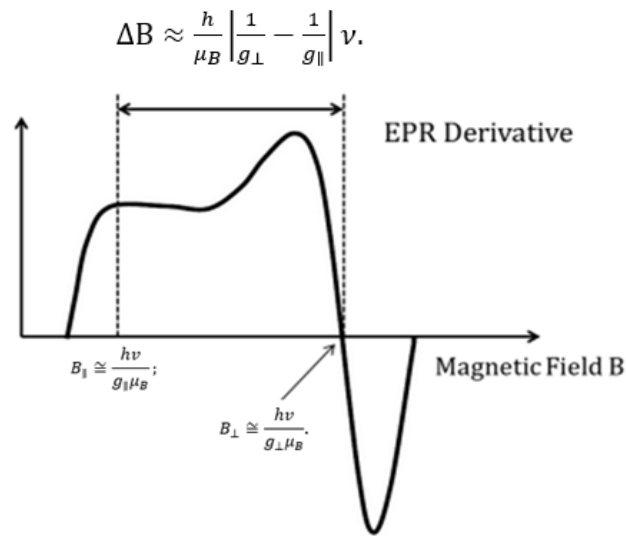


Figure 5. This is a schematic illustration of the relationship between the resonance frequency and the breadth of a magnetic resonance spectrum and frequency, if the width is determined by spin orbit coupling, that is to say, by the range of g . In this case, we illustrate for the simple case of an axially symmetric defect, but the principle can be extended to essentially any other defect with a linewidth dominated by g .

Thus, we should be able to obtain a (very rough) measure of the range of g by comparing spectra at high fields and frequency, for example, 9.5 GHz and about 0.35 Tesla with spectra taken at very low fields and frequencies, for example, 88MHz and 0.0032 Tesla. The low field and frequency spectrum will be significantly narrower than the high field spectrum if g is playing a significant role in the broadening and the difference in line width should provide a zero-order measure of the range in g , so long as other features, such as the hyperfine interactions, are approximately field and frequency independent.

I f A Comment: Near Zero Field Magnetoresistance Spectroscopy

This report also includes a very small contribution dealing with near zero field magnetoresistance (NZFMR) spectroscopy. This is very nearly unavoidable because some of our very low field EDMR measurements go down to zero field where this phenomenon is often obvious. We have funding on a separate DTRA contract to investigate this phenomenon. The project involves collaboration with Prof. Michael Flatte of the University of Iowa, and Prof. Nicholas Harmon of the University of Evansville. In an NZFMR measurement, no oscillating field is applied to the sample and the applied quasi-static field is generally quite small. The physical basis for NZFMR and EDMR are related. Both near zero magnetic field spin dependent trap assisted tunneling and spin dependent recombination currents are altered by the mixing of the same singlet and triplet states involved in the EDMR response. Instead of the magnetic resonance induced transformation of triplet to singlet states which cause the EDMR response, in NZFMR the triplet and singlet states are mixed when the field is close to zero. This response generally involves the same sort of electron-nuclear hyperfine interactions involved in conventional EPR as well as EDMR. A detailed explanation for NZFMR is fairly complex and not yet fully developed.

II. Experimental Equipment, Set Up and Procedures: Electrically Detected Magnetic Resonance (EDMR) and Conventional Laboratory Electronics Gear

The most important equipment utilized in this study were several EDMR spectrometers. The spectrometers operated at both high fields and frequencies and very low fields and frequencies. The high field/frequency spectrometers operate at X-band, about 9.5GHz and fields of around 0.3400 Tesla whereas the low field/frequency spectrometers operate at frequencies of 85 to 500MHz and fields of about 3 to 20 milliTesla. These X-Band systems are partly commercial systems and are partly home built, while our low-field and low-frequency EDMR spectrometers are completely home built. The majority of our EDMR measurements utilized two spectrometers. A representative X-band ($\nu \approx 9.6$ GHz) spectrometer includes a 4-inch Lakeshore electromagnet with a Micro-Now microwave bridge and a TE₁₀₂ cavity. A representative low frequency spectrometer ($\nu \approx 88$ to 500 MHz) consists of a set of custom-built Helmholtz coils, Kepco power supply, Lakeshore 475 DSP Gaussmeter and Hall probe, and several interchangeable Doty Scientific radiofrequency (RF) coils.

A Stanford Research Systems Low-Noise Current Preamplifier was utilized for both device biasing and current measurement at both high and low field/ frequency combinations. A Rigol DG1022 arbitrary waveform generator was used in the SDCP measurements. EDMR detection utilized a home-built virtual lock-in amplifier. The high and low frequency measurements were all carried out at room temperature. Schematic illustrations of the high and low field systems are illustrated in figures 6 and 7. Figure 8 provides a photograph of one of the low-field EDMR systems and illustrates device mounting for EDMR measurements. Figure 9 provides a more detailed cartoon of that specific system which includes details with regard to the sample mounting system.

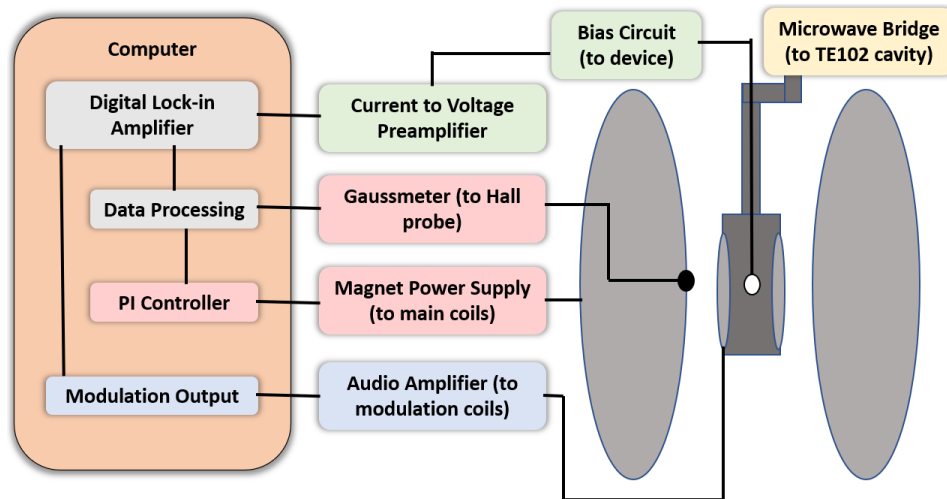


Figure 6. A schematic representation of an SDR spectrometer which operates at X-band, about 9.5GHz and magnetic fields of about 0.35 Tesla. The gray disks on either side of the microwave cavity and bridge represent the spectrometer's electromagnet.

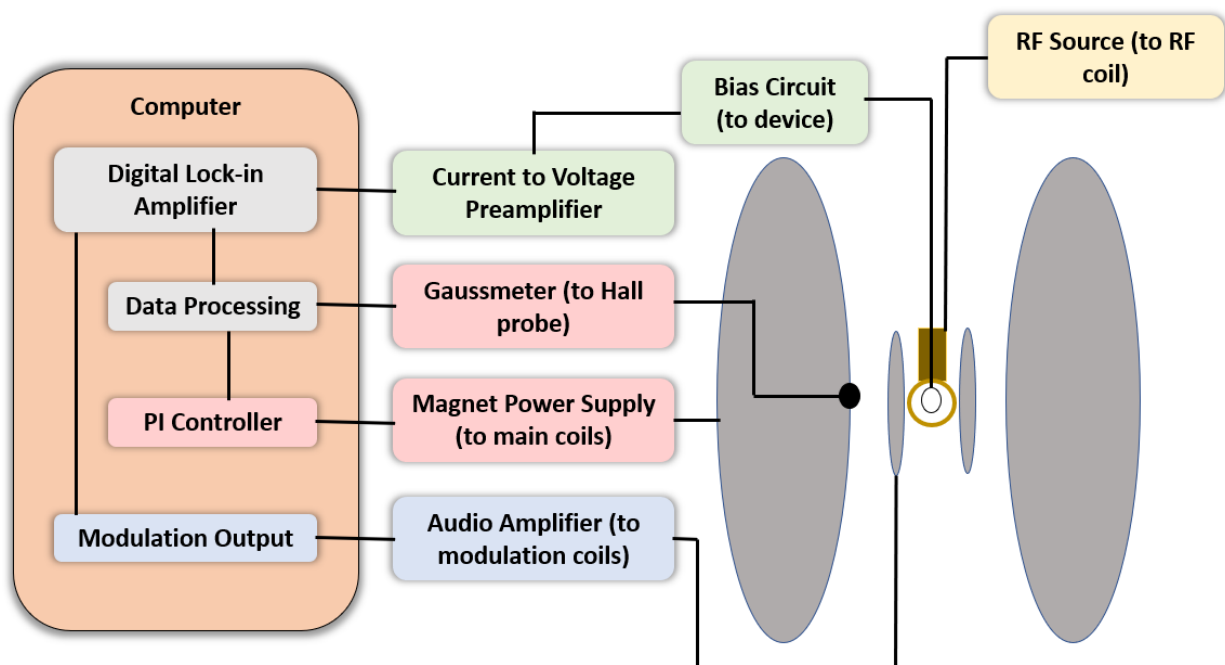


Figure 7. A schematic representation of a low field/frequency SDR spectrometer; 3 to 20 milliTesla, 87 TO 500MHz. The gray disks on either side of the RF source and coil represent the electromagnet, a set of nested Helmholtz coils.

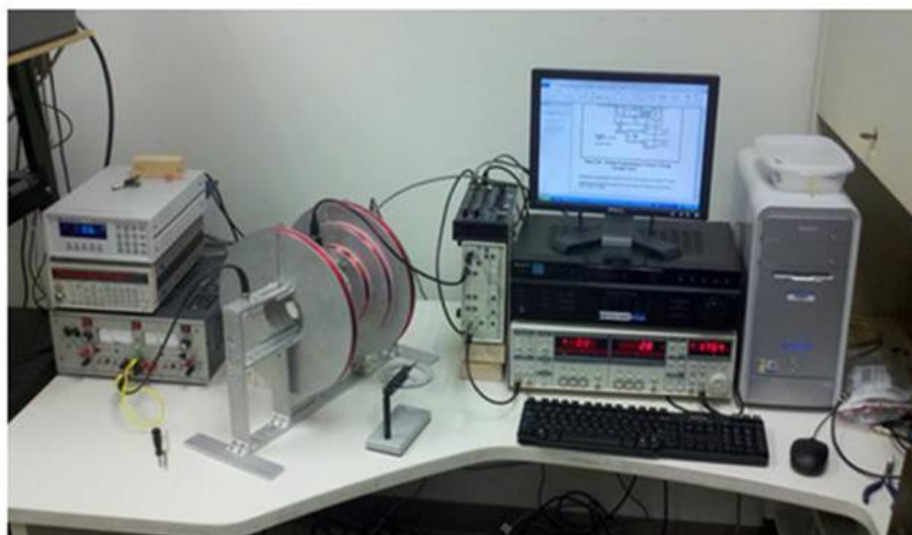


Figure 8. A low field EDMR spectrometer.

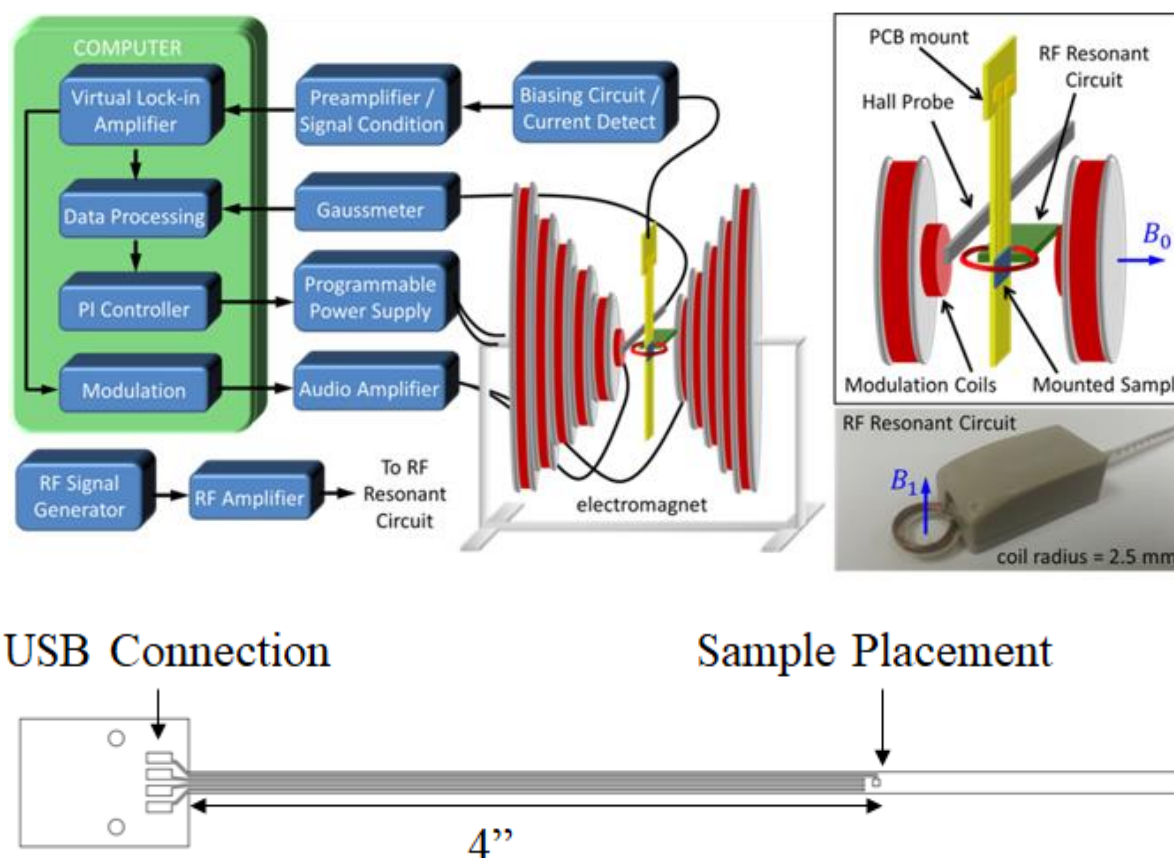


Figure 9. A schematic of the EDMR spectrometer in figure 8 with details of the sample mounting system shown on the right, with a second schematic of the PCB mounting system shown below.

It should be noted that, in addition to all of the magnetic resonance related apparatus, many other types of equipment were utilized in the study. We made straightforward electrical measurements utilizing standard electronic laboratory electronics: two commercial semiconductor parameter analyzers, commercial capacitance bridges and a homemade MOSFET charge pumping system. Sample mounting involved the use of a wire bonder.

III. Experimental Results: Electrically Detected Magnetic Resonance (EDMR) and Conventional Semiconductor Electronics Measurements

The primary focus of this study has been the utilization of EDMR to develop a fundamental understanding of the atomic scale defects in new and emerging devices and materials for space applications. The study utilized the techniques and the apparatus described in sections I and II. Our work included: EDMR studies of:

Tri-Gate Metal Oxide Silicon Devices (often called FinFETs)

Low Dielectric Constant (SiOC:H) Interlayer Dielectrics

HfO₂ Based Resistive Random-Access Memory (RRAM) Devices

Silicon -Germanium based Metal Oxide Silicon Field Effect Transistors

III a Tri-Gate/ FinFET Device Studies

Recently, multi-gated metal oxide semiconductor field effect transistors (MOSFETs) have become the dominant devices in high-performance CMOS integrated circuits. Investigations of tri-gate devices are generally of interest. This is so for several reasons but, most importantly, tri-gate, or FinFET, devices greatly reduce short channel effects, allowing improved scalability [13].

We obtained FinFET / Tri-Gate devices from two sources. One industrial R and D center asked that we not subject the devices to gamma irradiation. The other source, a university laboratory had no objection to irradiating their devices. Therefore, we report on gamma irradiated devices as well as on negative bias temperature (NBT) stressed devices. Both the negative bias temperature instability (NBTI) and radiation damage involve the creation of positive oxide charge and silicon/ dielectric interface trap generation. Although the analogy is not perfect, we hope that our substitution of NBT stressing of some of the devices will be deemed reasonable. Also, there is little literature dealing with the atomic scale defects involved in any reliability problems, including radiation damage and NBTI in such devices.

Our EDMR measurements in both studies utilized both high and low field/ frequency EDMR spectrometers as discussed earlier in this report. Measurements were conducted at room temperature.

In the first FinFET/ Tri-gate study, we utilized (100) silicon-on-insulator (SOI) FinFETs, provided through a university laboratory. The modified transistor is processed from 90 nm Si on a 125 nm buried oxide. Above the oxide are n⁺/p-/p⁺ fins with a channel lengths, heights, and widths of 500 nm, 80 nm, and 50 nm, respectively. The “body” region of these devices is lightly doped p-type to $2 \times 10^{15} \text{ cm}^{-3}$. The FinFETs are gated with 1 nm SiO₂ and 2 nm HfSiON/TiN/polySi-capped gate stacks, realizing an effective oxide thickness of approximately 1.1 nm. Additionally, the (100) face

of the fin has a spacer formed on top of the gate oxide in order to effectively create a double-gate device. The sidewalls of each fin are formed on the (110) plane of the silicon channel. For one set of gate/n+/p+ contacts, 500 fins are wired in parallel. The structure is schematically illustrated in figure 10. We irradiated the FinFETs under study to 1 Mrad (air) with a ^{60}Co gamma source with a gate bias of +0.9 V applied during irradiation.

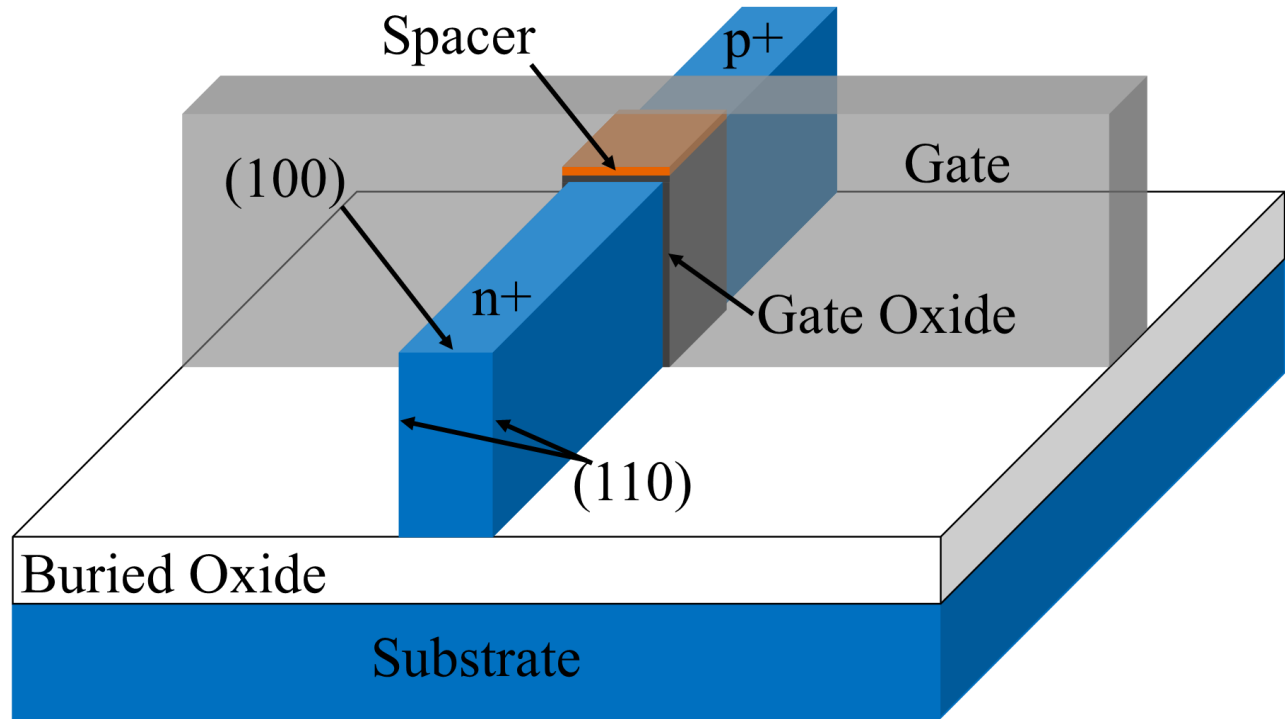


Figure 10. Cartoon diagram of the gated diode FinFETs used in the study.

In order to determine changes in interface state density in the FinFETs, we compared DCIV curves pre- and post-irradiation. Changes in the peak recombination current account for an increase in interface state density to $N_{\text{IT}} \approx 1.54 \times 10^{11} \text{ cm}^{-2}$, with a pre-irradiation density $N_{\text{IT}} \approx 1.25 \times 10^{11} \text{ cm}^{-2}$. Although the differences in interface trap density were modest, the differences in EDMR spectra were dramatic. We compare the pre- and post-irradiation X-band spectra with the magnetic field parallel to the (100) plane in Fig. 11. There are no observable EDMR responses in the pre-irradiation traces, but in both SDR and SDCP we see gross changes in the devices after irradiation. For both measurements, only a single, broad line is observed with $g = 2.005 \pm 0.001$ and a linewidth of approximately 24 Gauss. A comparison of the 0° and 90° orientations is shown in Fig. 12. Although the EDMR response of planar Si/SiO₂ shows significant differences between these orientations, we observe very little to no difference in the zero-crossing g and linewidth.

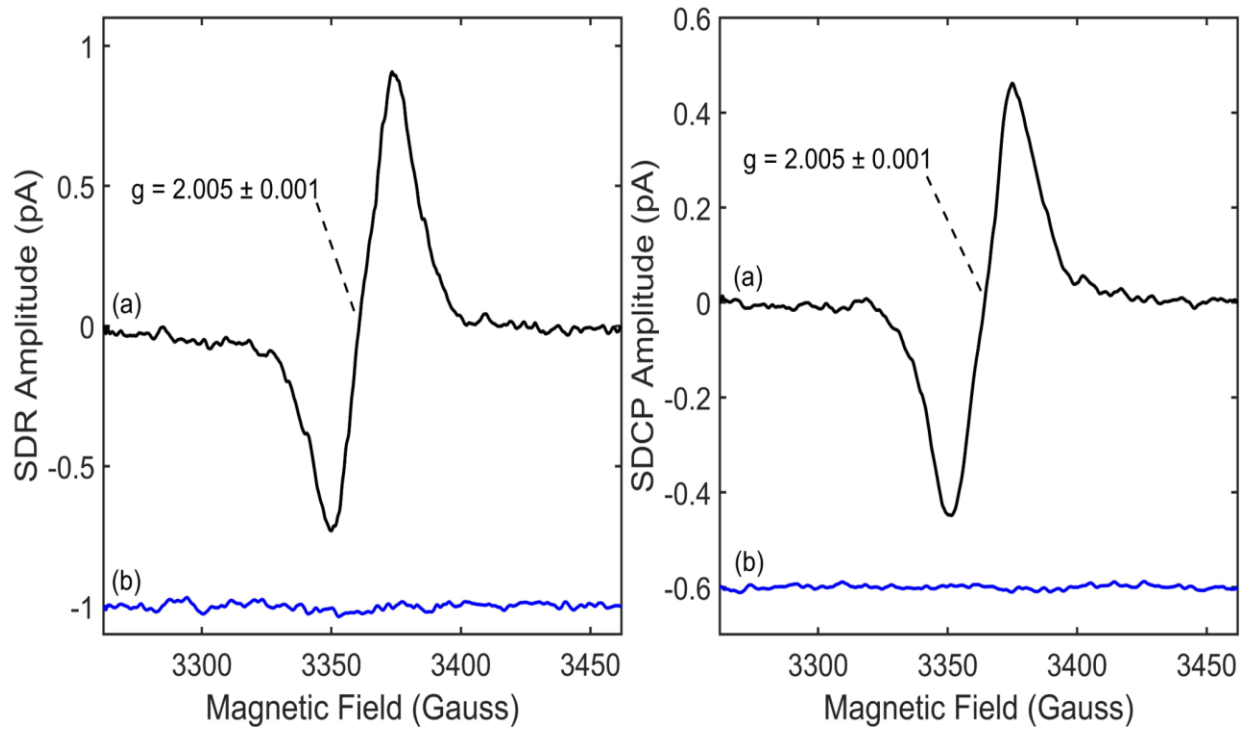


Figure 11. SDR (left) and SDCP (right) EDMR taken at high field/frequency ($\nu \cong 9.5$ GHz) for both (a) post 1 Mrad irradiation and (b) pre-irradiation. The dotted line corresponds to the zero-crossing g value and its location on each spectrum.

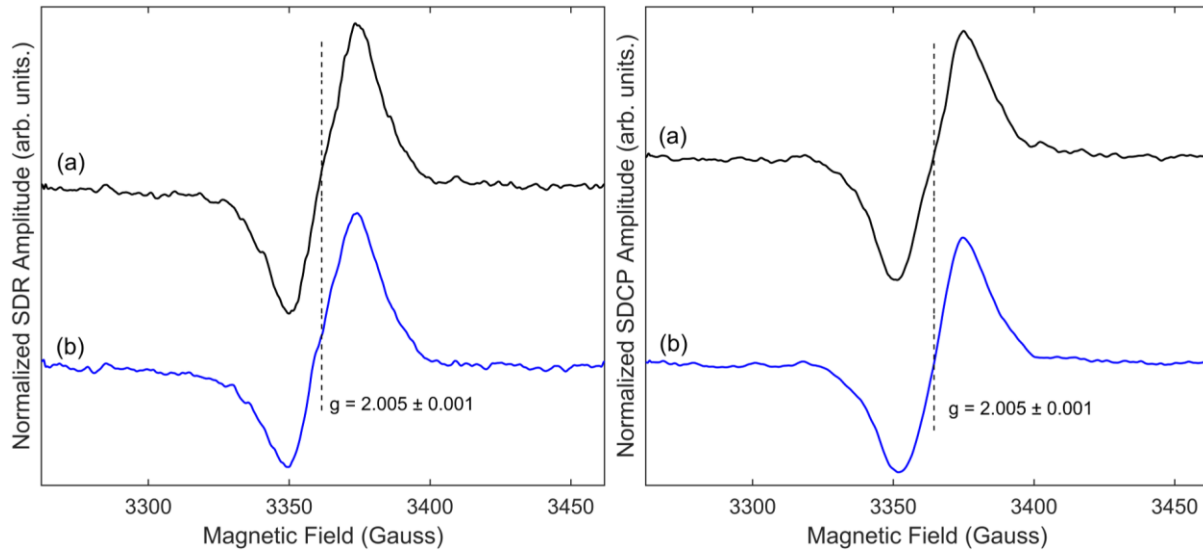


Figure 12. SDR (left) and SDCP (right) EDMR taken at high field/frequency ($\nu \cong 9.5$ GHz) on a FinFET irradiated to 1 Mrad with (a) the (100) plane parallel to the magnetic field and (b) perpendicular to the magnetic field. The vertical axes have been normalized for a clear comparison. The dotted line is in reference to the zero-crossing g value and its location on each spectrum.

We compared these high field results to EDMR measured at low field. As the field and frequency are lowered, as discussed previously, contributions from spin-orbit coupling collapse. As discussed in section Ie, multi frequency EDMR, additional information about the defects observed in these spectra can be obtained by comparing the high field/frequency EDMR results to similar measurements made at low field/frequency. As discussed previously, the high and low field/frequency comparison allows one to approximately determine the breadth of g tensor components, Δg , giving insight into the contributions of spin-orbit coupling in the high field spectra. This is because line broadening resulting from spin-orbit coupling is directly proportional to the field/frequency at which the EDMR measurement is made,

Making the approximation that $g_{\parallel} \approx g_{\perp} \approx 2$,

$$\Delta g \approx \frac{4\mu_B}{h} \left(\frac{\Delta B_{high} - \Delta B_{low}}{\nu_{high}} \right), \quad (10)$$

where ΔB_{high} and ΔB_{low} are the spectra's linewidths at high and low field, respectively, and μ_B and h have been previously defined.

Using $\nu = 378.1$ MHz and a resonance field of approximately 135 Gauss nearly all broadening due to g is removed. Fig.13 plots spectra from both high and low fields. Comparing the two lines, we compute broadening due to g . As with the high field spectrum, the low field trace is featureless, but with a much smaller width of only 4 Gauss. The difference between the high and low field linewidths is 20 Gauss. The range of g covered by the P_b family of defects on either the (100) and (110) interfaces extend from 2.0012 to 2.0081, [13] which corresponds to approximately 12 Gauss. If the nearby E' center is also being observed in these measurements, then the Δg calculation broadens slightly to 13 Gauss.

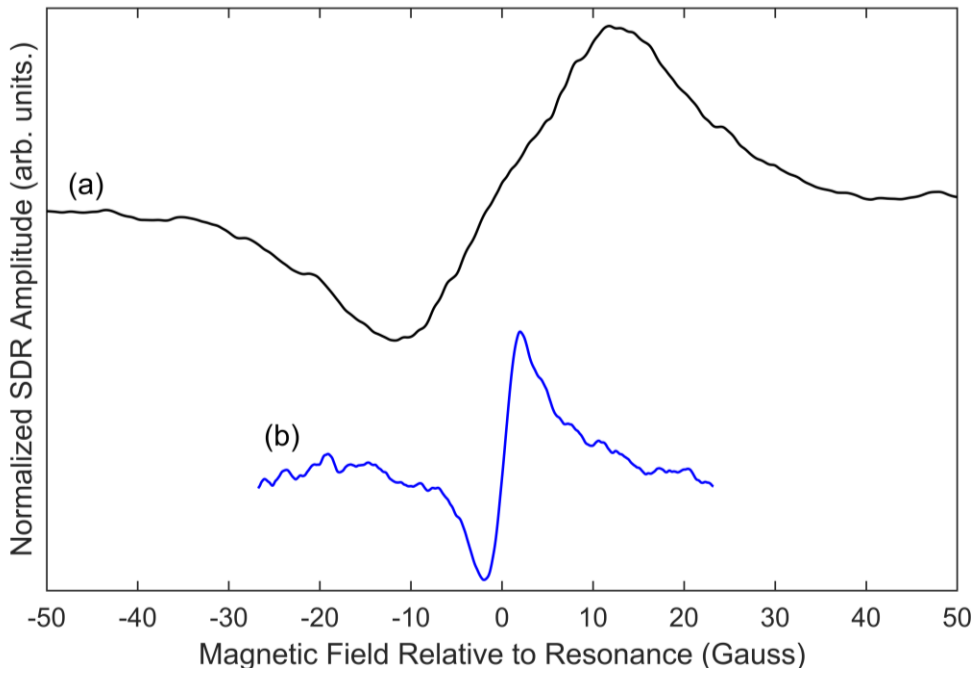


Figure 13. SDR EDMR taken on a FinFET irradiated to 1 Mrad at (a) high field/frequency ($\nu \cong 9.5$ GHz) and (b) low field/frequency ($\nu = 378.1$ MHz). The spectra have been shifted in order to align the zero-crossing of the lines and the vertical axes have again been normalized.

The zero-crossing g values for the radiation-induced interface defects EDMR is about what one would expect for a randomly oriented array of P_b centers, about 2.005. (Remember that in planar devices we observe a range from 2.0012 to 2.0081.) [13] However, the high-low field/frequency comparison indicates that the range of g involved is somewhat larger than anticipated for P_b centers, based on expression (10). We conclude that the radiation-induced interface traps observed in these FinFETs are similar to, but not quite the same as, the radiation-induced interface traps observed in simple planar Si/SiO₂ devices. Of perhaps far greater interest, the irradiation only moderately increased the interface trap density. Although quite strong EDMR traces appear after irradiation, no EDMR response was detected prior to irradiation. This result indicates, at least in the FinFETs utilized in this study, that the as-processed interface traps have a physical origin different than the radiation-induced defects. In conventional planar Si/SiO₂ devices, the interface traps in as-processed devices are generally also P_b centers [13]. (This observation will require further investigation.)

It is important to realize that these EDMR results do not completely elucidate the FinFET radiation damage process. One question worth addressing is whether the radiation damage process involves the alteration of a defect charge state or the creation of a new defect or some combination of both possibilities. It is likely that reality involves some combination of the two. For example, the capture of a hole at a near-interface E' center creates an EPR response. The hole capture event renders the site paramagnetic, that is, EPR active. This capture event creates an odd number of electrons at the

defect site. The odd number is what makes the site EPR active. In EDMR, one observes the resonance response via repeated changes in defect charge state. One might therefore conclude that a process involving a change in defect charge state could not alter the EDMR. This is not necessarily the case. The E' sites provide a good illustration of this possibility. The initial radiation-induced hole capture event results in a significant structure change at the site which may or may not recover [13]. If the recovery process does not take place and the E' center is close to the Si/SiO₂ interface, the defect may become a “border trap” or “switching trap”, that is, a defect which may respond (slowly) to changing positions of the near-interface Fermi level [13]. It is possible that some of the FinFET EDMR response is in fact due to such border traps in the relatively slow DCIV EDMR measurements. The E' boarder trap response would likely only account for a small fraction of the DCIV EDMR response because the observed spectrum is very wide (~24 Gauss). Typically, E' spectra are quite narrow at only a few Gauss wide.

The second FinFET/ Tri-gate study utilized three types of devices. In this study, we utilized one planar device and two tri-gate Si pMOSFET test structures supplied by an industrial research and development center. One goal in this study was to evaluate whether our conclusions in the first study with regard to slight differences in the defect structure between planar devices and FINFETs are generally the case or an artifact of the samples in the initial study. All devices in the second study have 40μm channel lengths with a gate stack containing a thin layer of SiO₂ followed by a HfO₂ and a TiN metal gate. The oxide processing was essentially identical for all three sets of devices. The planar MOSFET has a 5 μm channel width. The tri-gate FETs contain 41 nm and 300 nm channel widths with a 40 nm fin height surrounded by a high-k metal gate. The fins have (110) sidewalls and a (100) top face. Each set of contacts contains either 66 (41 nm width) or 7 (300 nm width) fins wired in parallel with the substrate electrically connected to each fin. As mentioned previously, the organization which provided these devices explicitly requested that we not subject them to ionizing radiation; therefore, these measurements involved negative bias temperature gate stressing. The devices were stressed with a gate bias of -1.9Vg at 140°C. Fig. 14 shows that the NBTI-stress has significant impact on the electrical characteristics of the 300 nm wide tri-gate device. In the IDVD measurements (Fig.14, left) the stress has reduced the drain current at a gate bias of -0.85 V by approximately one order of magnitude. The effects of the stress can also be noted in the Elliot curves (Fig. 14, right). The peak of the charge pumping current indicates about a doubling in interface trap defect density and a shift in the location of the post-stress peak which suggests the building of charge within the dielectric.

Fig. 15 and Fig.16 display the results of SDCP on both pre- and post-stress 300 nm wide tri-gate devices. For SDCP optimal signal-to-noise, the amplitude of the charge pumping waveform was increased to 1 V_{pkpk}. Fig. 15 shows a large difference in pre- and post-stress signal size. Fig. 16 shows that the overall shape of the SDCP response is similar between the pre- (left) and post-stress (right) devices. The g-values for both the pre- and post-stress signals are consistent for their respective orientations ($g_{\parallel} \approx 2.0061$ and $g_{\perp} \approx 2.0051$). While the lines maintained both shape and g-value, the amplitude increased in size by nearly an order of magnitude. This indicates that while a substantial number of defects are being generated in the NBTI process, they are physically and chemically similar.

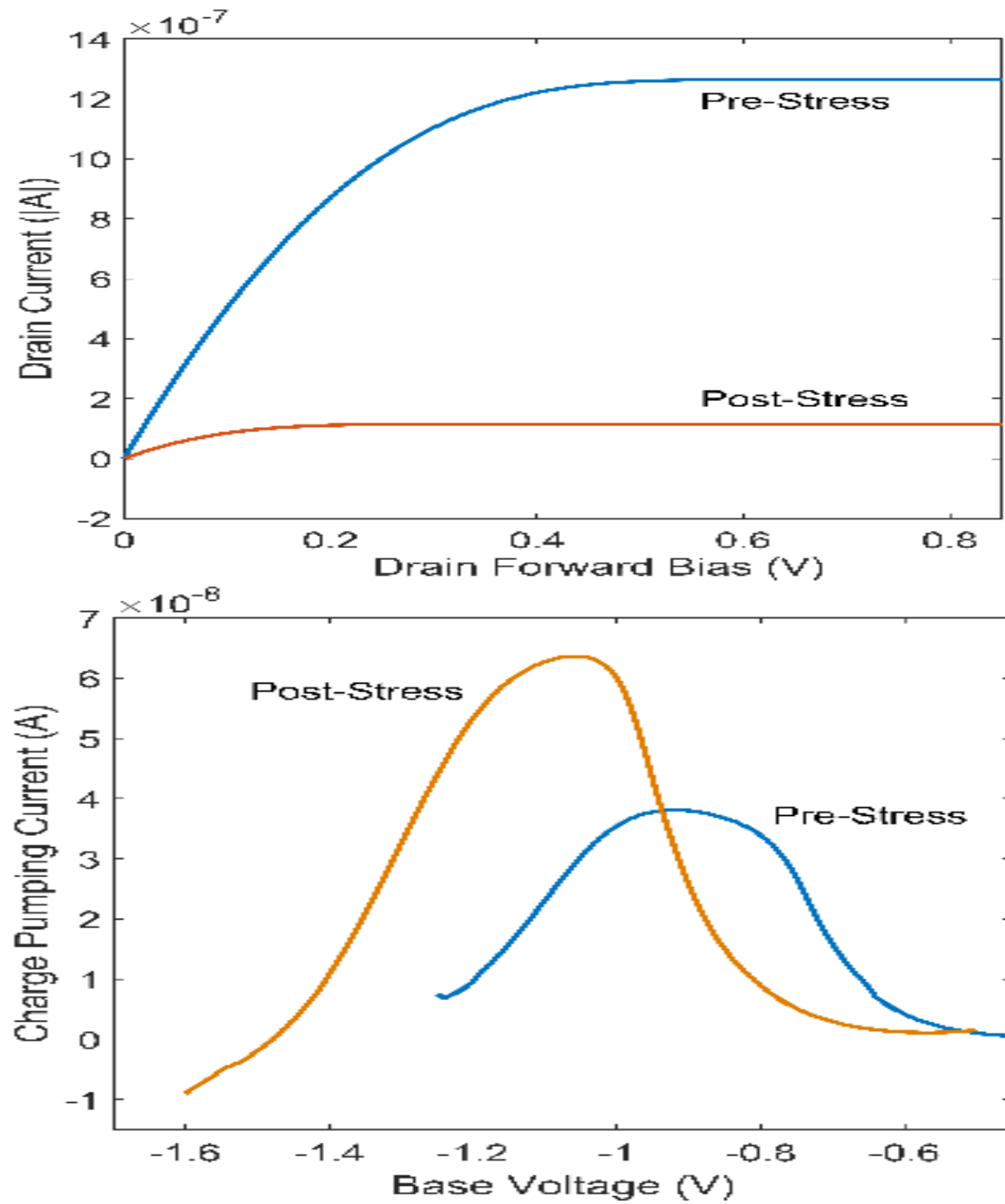


Figure 14. (left) Pre- and post-stress comparison of IDVD curves at $-0.85 V_G$. (right) Pre- and post-stress comparison of Elliot curves. These curves were taken on the 300 nm wide devices. The applied waveform is $0.8 V_{pkpk}$ at 285 kHz with 350 ns rise and fall times.

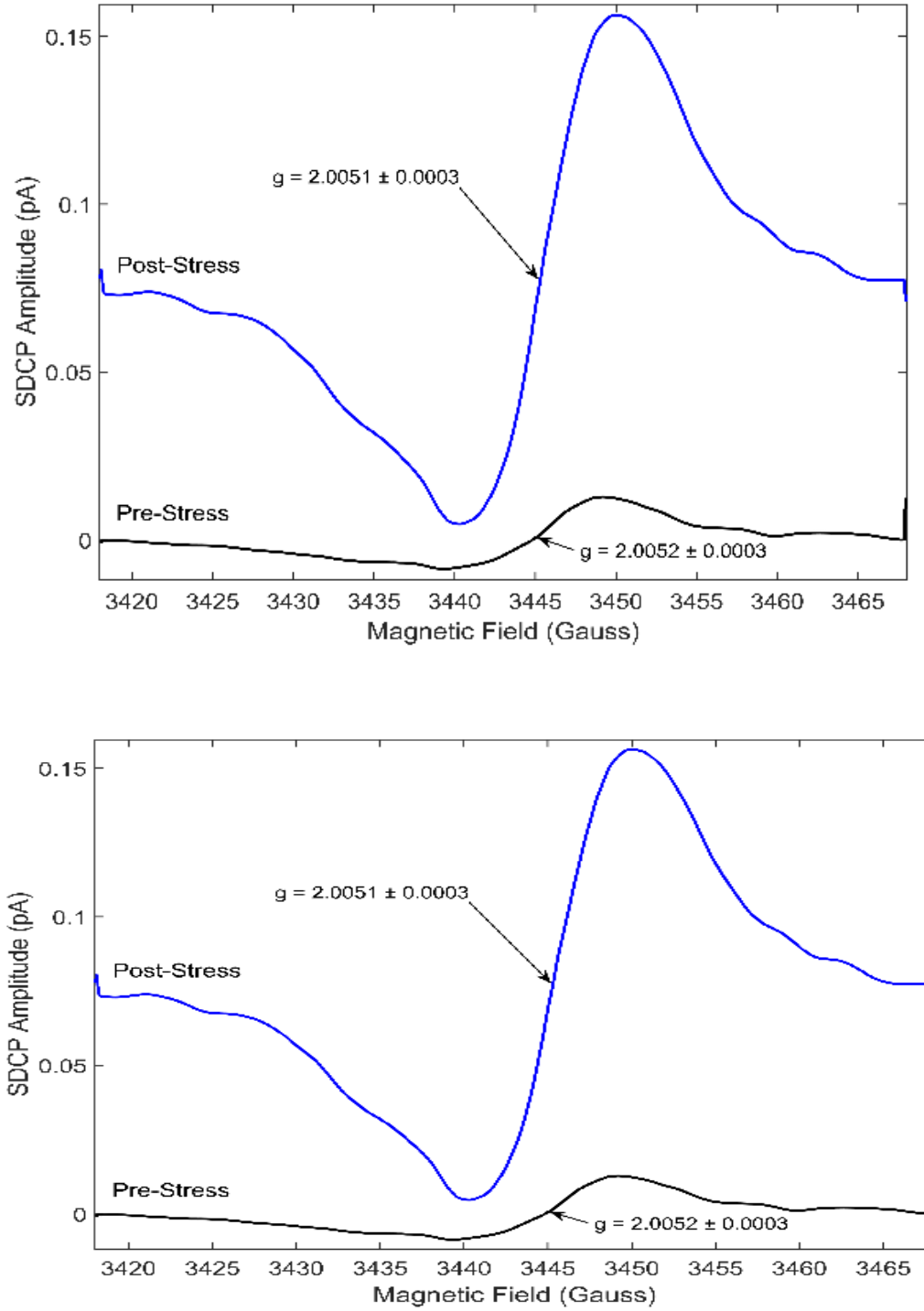


Figure 15. A comparison of SDCP signals taken on pre- and post-stressed 300 nm wide tri-gate devices with the magnetic field oriented parallel to the (100) interface plane of the wafer, as well as parallel to the top plane of the FinFET.

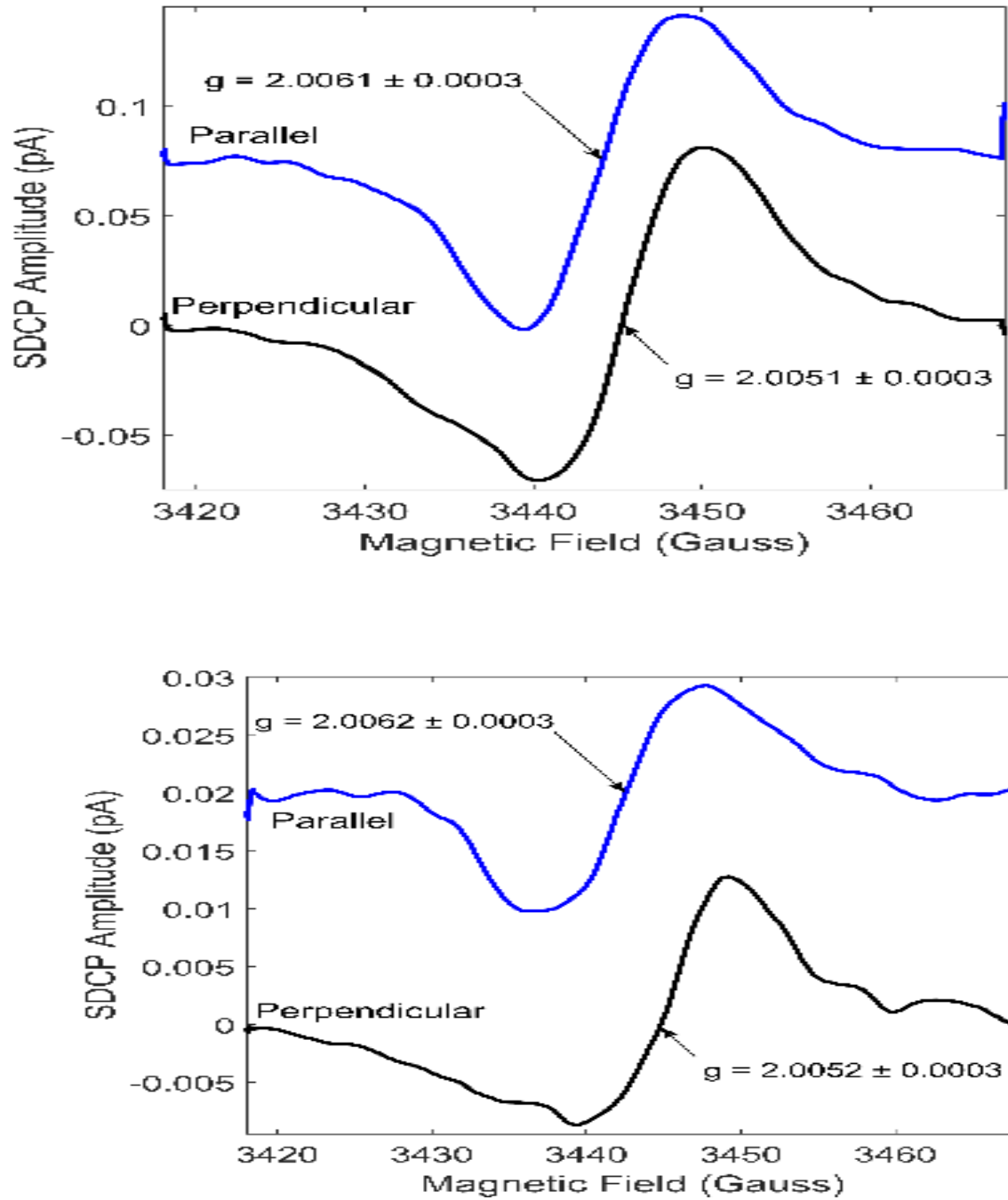


Figure 16. (Top) Pre-stress comparison of the 300 nm tri-gate device's SDCP signals with the device rotated 90° with respect to the magnetic field. (Bottom) Post-stress comparison of SDCP signals with the same orientation scheme. The trace amplitudes were normalized so as to make the close similarities in the spectra clearer to the reader

Comparisons of all three device types' post stressing X-band spectra at both orientations are shown in Fig. 17. In this figure, differences in orientation dependence are observed between the planar, 300nm wide fins, and 41nm wide fins. The planar device shows the most significant orientation dependence with zero-crossing g -values ranging from $g_{\parallel} \approx 2.0057$ to $g_{\perp} \approx 2.0038$. The observable dependence in the planar device EDMR is consistent with the fairly high level of order at the Si/SiO₂ interface in these devices. However, in both tri-gate cases, the differences in EDMR with respect to orientation are less dramatic. This is evident in the spectra from both the 300 nm and 41 nm wide fins. In the 300nm device, the spectra have significantly reduced orientation dependence with g -values of $g_{\parallel} \approx 2.0061$ to $g_{\perp} \approx 2.0051$. In the case of the 41 nm device, the difference in zero crossing g is within experimental error, likely due to the reduced (41 nm) channel width and shape of the fin.

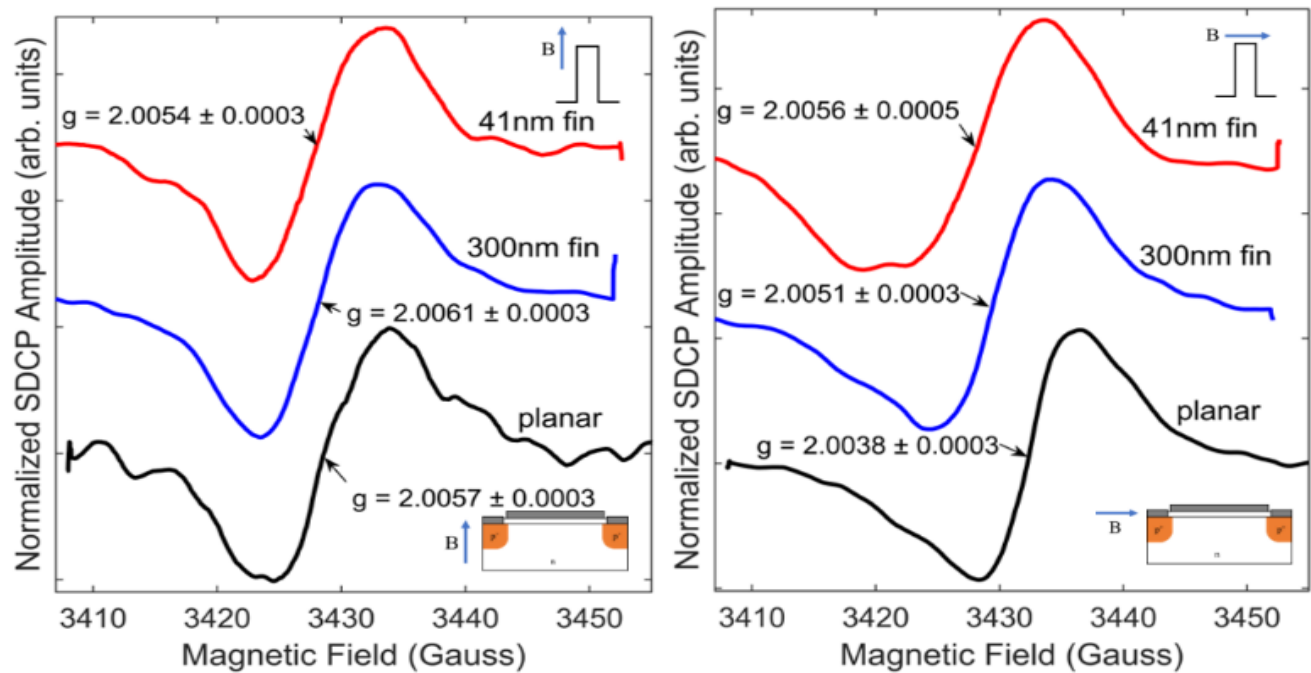


Figure 17. A comparison of X-band SDCP signals taken on all three post-stress devices for both the (left) “parallel” and (right) “perpendicular” orientations. Note the difference in g -values for each device.

The high field/frequency EDMR spectra reported herein are somewhat different from those found in a previous study of NBTI in planar Si/SiO₂ MOSFETs [14]. In that study, it was found that P_b centers, Si dangling bonds at the Si/SiO₂ interface, are the dominant defect in NBT-stressed devices. In terms of the g tensor components and signal width, these spectra are similar, but not exactly the same as those observed by Campbell *et al.* [14] for either of the tri-gate devices. Since the EDMR spectra are quite similar to those expected from P_b centers, the results most strongly suggest that the tri-gate interface defects are P_b -like, but may be somewhat more complex than those in conventional planar devices.

Additional evidence in this regard is again provided by high/low field frequency EDMR comparisons. As we did with the first set of FinFETs, we again compared the high and low frequency EDMR responses. In Figure 18, we illustrate low field and frequency EDMR on these samples. Using an RF coil at 88.3 MHz corresponds to a resonance field of approximately 32 G. As previously mentioned, nearly all broadening due to g tensor components is removed at this low of a field. Fig.18 shows that the resonance linewidth has been reduced to about 2.5 G in all three device types from about 9 G in the high field/frequency measurements. This corresponds to approximately 6.5 G broadening from low to high fields/frequencies. Again, following the analysis of expressions 8, 9, and 10, discussed previously, we find that the difference in broadening fits well within what one could expect for a range of P_b centers, corresponding to a Δg of 0.0039. These results again strongly support the conclusion that the defects observed in the EDMR spectra in these tri-gate devices are P_b -like. However, these results do not provide significant evidence for greater complexity in the tri-gate devices than in the planar devices.

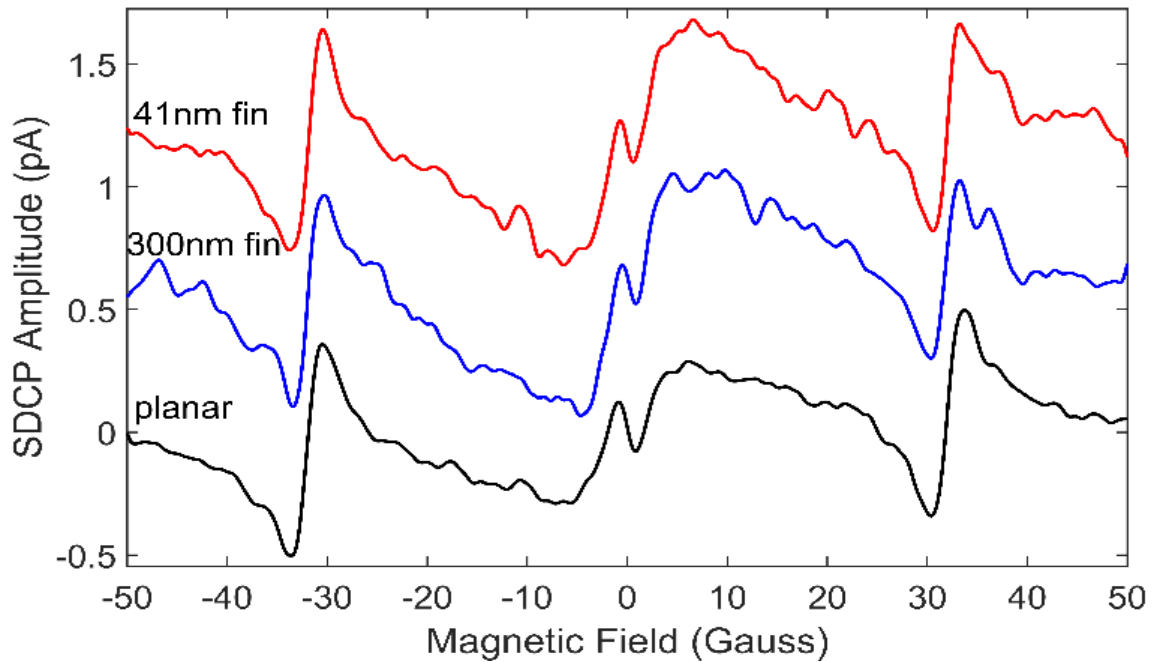


Figure 18. A comparison of SDCP signals taken on all three post-stressed devices at low field/frequency. The resonance peaks are located at approximately ± 32 G. The peak positions are consistent with EDMR detection at 88.3MHz

Conclusions About the Tri-Gate Device Oxide/Silicon Interface Traps

Our studies of Tri-Gate devices provided by two independent sources, with two different types of stressing, both indicate that the defect populations in the planar and tri-gate devices are very similar to the defect populations at the oxide/silicon interfaces of planar devices. Our results provide more tentative evidence that modest differences may exist between planar and FinFET oxide/ silicon interfaces.

III.b Low Dielectric Constant (SiOC:H) Interlayer Dielectrics

Leakage currents in low dielectric constant, so called low- k dielectrics, [15,16] thin films utilized in present day integrated circuitry are an important reliability concern. In this study, we have explored the response of dense and porous a-SiOC:H thin films to ionizing radiation. There are several key differences in processing between the dense and porous films; a porogen is introduced during the deposition of the porous films, this porogen is later removed with a UV treatment and anneal. Our results, although preliminary, suggest that, in spite of these different processing requirements, the atomic scale mechanisms appear to be quite similar. Although our observations are focused upon radiation damage, we believe that they may be of broader relevance to reliability issues in low- k systems, for example stress induced leakage current. The ionizing radiation significantly changes leakage currents depending upon biasing conditions during irradiation. This change is accompanied by changes in electrically detected magnetic resonance (EDMR) and low field magnetoresistance (MR) measurements.

We have initiated a study in which we subject metal-insulator-silicon structures to 15 Mrads of ^{60}Co gamma irradiation. The films studied include 56 nm dense a-SiOC:H films and 17 nm porous a-SiOC:H films. During irradiation, the dense films were subjected to biasing corresponding to $\pm 2\text{MV/cm}$ and no bias, and the porous films were subjected to biasing corresponding to -1.2MV/cm , $+0.75\text{MV/cm}$, and no bias. We define polarity as the sign of the bias applied to the metal.

In Fig. 19 we illustrate current versus voltage curves taken on dense a-SiOC:H films before and after subjecting them to 15 Mrads. We observe a large increase in leakage current for samples irradiated with a bias of $+2\text{MV/cm}$; however, we observe a suppression of leakage current for the samples irradiated with either a bias of -2MV/cm or no bias. Figure 20 illustrates a representative comparison of low field (frequency $\sim 150\text{ MHz}$) and X band (frequency $\sim 9.75\text{ GHz}$) EDMR measurements made on the films before gamma radiation and Fig. 21 illustrates a similar measurement taken after gamma radiation at -2MV/cm . Figure 20 shows a very large difference in the high and low frequency EDMR traces prior to irradiation while Fig. 21 illustrates a significantly smaller difference in the high and low frequency line widths after irradiation. In Fig. 20 and Fig. 21, a significant change in the zero-crossing g is also evident; prior to irradiation, $g=2.0029$ and after irradiation $g=2.0055$.

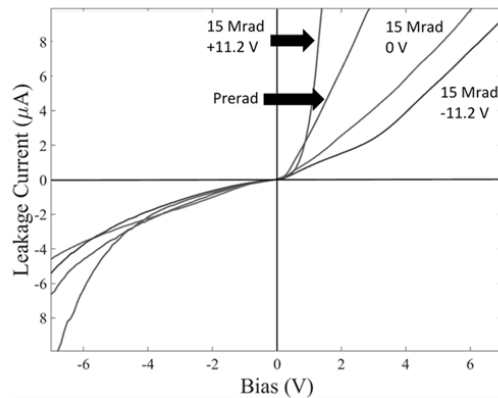


Figure 19. Current-voltage measurements made on dense a-SiOC:H films pre-and post-irradiation.

Figures 22 and 23 illustrate similar comparisons on quite different porous oxides. As is the case for the dense oxides, the pre-irradiation zero-crossing g is $g=2.0029$. After irradiation, the g increases to $g=2.0049$; this is very nearly within experimental error (± 0.0002) of the post-irradiation g in the dense oxides. Again, there is a large difference in the high and low field line widths prior to irradiation but a smaller difference in the widths of the post-irradiation curves. These results clearly demonstrate a significant physical difference in the nature of leakage current defects induced by the irradiation. The close correspondence between the thicker dense and thinner, porous dielectric data also strongly suggests similar physical phenomena.

Additional, but unfortunately not absolutely definitive, insight can be gleaned from the high/low field-frequency comparisons. As recently discussed by Mutch *et alia*, [17] one can utilize a comparison of high and low frequency EDMR measurements to determine the breadth of defect g tensor components.

The broadening due to the distribution of g tensor components is proportional to the field and frequency at which the resonance occurs. The mechanism can be readily understood for the simple case of an axially symmetric defect in an amorphous or polycrystalline matrix in which nearly all of the line width is due to g tensor components. This line shape has a well understood shape and width corresponding to the range of g tensor components. The approximate lower-field and higher-field cut off responses are respectively:

$$B_{\parallel} \cong \frac{h\nu}{g_{\parallel}\beta} \quad (5)$$

$$B_{\perp} \cong \frac{h\nu}{g_{\perp}\beta}. \quad (6)$$

From these equations,

$$\Delta B \approx \frac{h}{\beta} \left| \frac{1}{g_{\perp}} - \frac{1}{g_{\parallel}} \right| \nu \quad (7)$$

Since $g_{\parallel} \approx g_{\perp} \approx 2$,

$$\Delta B \approx \frac{h}{\beta} \left(\frac{\Delta g}{4} \right) \nu \quad (8)$$

We can use (8) to solve for Δg in terms of high and low frequency EDMR line widths, ΔB_{high} and ΔB_{low} , as follows:

$$\Delta g \approx \frac{4\beta}{h} \left(\frac{\Delta B_{high} - \Delta B_{low}}{\nu_{high}} \right). \quad (9)$$

A comparison of the pre- and post-irradiation results for both the dense and the porous films indicates a significantly broader range of g tensor components in the pre-irradiation samples. From the results of Fig. 20 and Fig. 22, we measure a $\Delta g=0.0044 \pm 0.0004$ prior to irradiation. After irradiation in Fig. 21 and Fig. 23, we measure a $\Delta g=0.0023$. Note that this change is approximately the same for the dense and porous results.

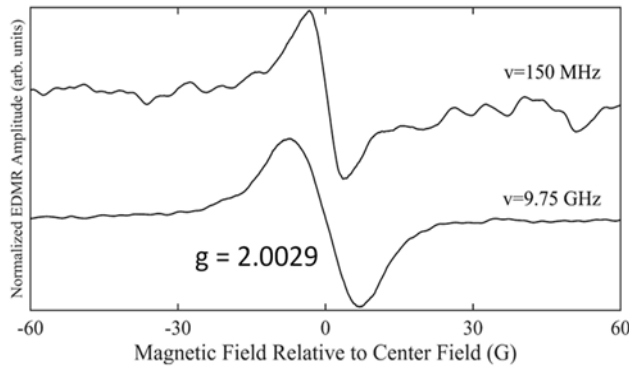


Figure 20. Low frequency EDMR traces compared to high frequency EDMR traces for pre-irradiation dense a-SiOC:H films.

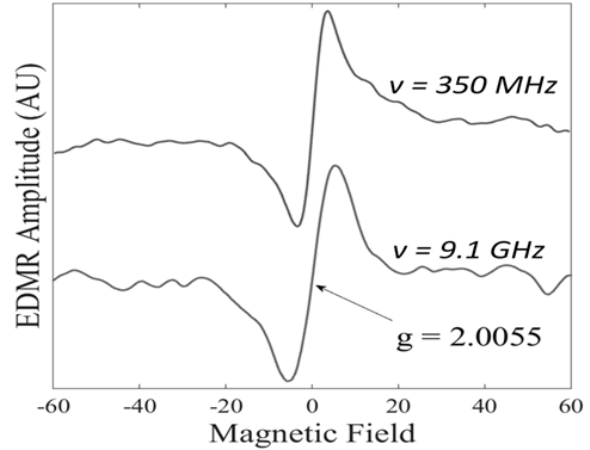


Figure 21. Low frequency EDMR traces compared to high frequency EDMR traces for the post-irradiation dense a-SiOC:H films.

Although this change in g tensor components and zero-crossing g values demonstrates a fundamental change in defect structure, the results do not yet allow an unambiguous assignment of the defect structure.

The values and distribution of g tensor components depend on spin-orbit coupling and defect energy levels. It is thus often possible to glean physical and chemical information about defects from this information. Unfortunately, the information is not without ambiguity. As discussed previously, a standard perturbation theory calculation relates the g tensor components to defect physics, for example in dangling bonds, [5] as follows:

$$g_{ij} = g_e \Delta g_{ij}, \quad (3)$$

Where

$$\Delta g_{ij} = -2\lambda \times \sum_{ij} \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0} \quad (4)$$

Here, g_e is the free electron g value, and Δg_{ij} is the deviation of the respective tensor component from g_e . The atomic spin-orbit coupling constant is λ , and i and j correspond to the principle axes directions. Since λ depends on the charge in the nucleus and the electron wave function, chemical and physical information may be obtained from the measurement. Unfortunately, the denominator terms ($E_n - E_0$) take into account energy level difference with respect to the observed paramagnetic state energy. Therefore, only limited conclusions may be drawn from this measurement. One may clearly conclude that a significant change in Δg means a significant change in defect structure. However, one might more tentatively conclude that in a comparison such as those illustrated in Figs. 20 and 21 and Figs. 22 and 23 indicating a large Δg in the pre-irradiation curves and a small Δg from the post-irradiation curves would indicate that a smaller atom (presumably C versus Si) is involved in the post-irradiation case because the smaller atom would lead to a smaller λ . However, such a conclusion is not conclusive because significant differences in the $E_n - E_0$ terms could play an important role in determining these values.

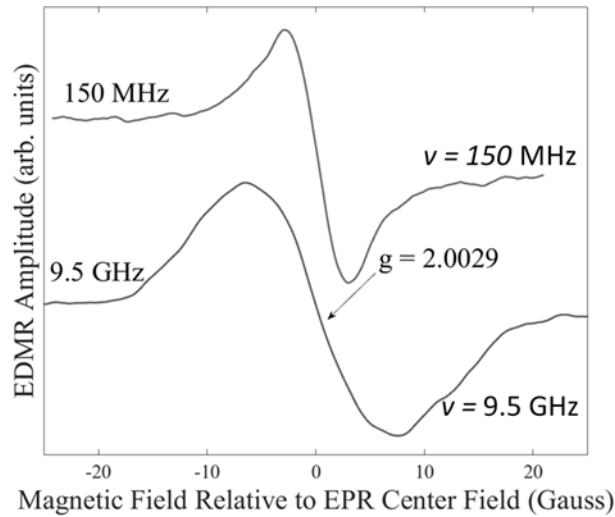


Figure 22. Low frequency EDMR traces compared to high frequency EDMR traces for pre-irradiation porous a-SiOC:H films.

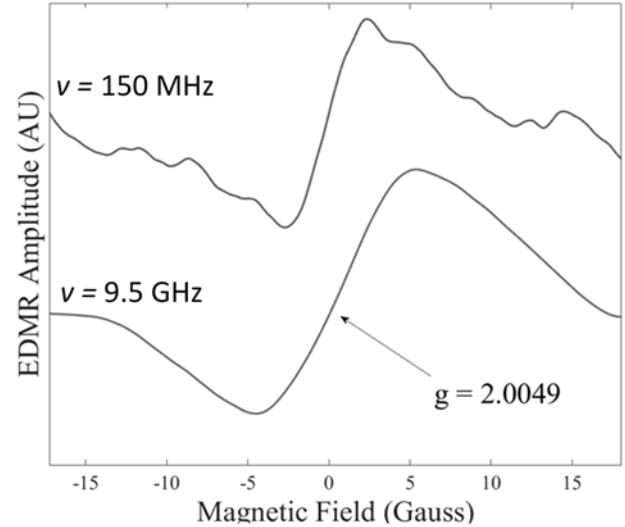


Figure 23. Low frequency EDMR traces compared to high frequency EDMR traces for post-irradiation porous a-SiOC:H films.

Conclusions with regard to the low-K dielectrics

In conclusion, our results suggest that both multiple frequency EDMR and the very simple near-zero field MR have promise as atomic scale probes of leakage currents in low- k dielectric films. Our results clearly demonstrate that the gamma irradiation significantly changes the physical and chemical nature of defects involved in the leakage currents for both dense and porous a-SiOC:H. This conclusion drawn from a comparison of high and low frequency SDTAT/EDMR spectra should be regarded as reasonably conclusive. A much more tentative conclusion drawn from our results suggests that the smaller Δg observed in the post-irradiation spectra is suggestive of a change from Si dangling bonds to C dangling bonds.

III c HfO₂ Based Resistive Random-Access Memory (RRAM) Devices

As flash memory reaches its practical scaling limits, resistive random-access memory (RRAM) offers potential advantages for future memories. These advantages include dense memory configurations, large “SET-RESET” cycles, simple integration with complementary metal oxide semiconductor (CMOS) technology, short switching times, and potentially high resistance to certain types of radiation [18]. However, at the present time there is virtually no direct experimental evidence identifying electrically active defects involved in RRAM radiation damage [19]. Furthermore, although many reasonable models have been proposed, there is also very little direct experimental evidence elucidating the underlying atomic scale conduction mechanism within RRAM devices under any circumstances. Although many different materials systems are under development for use in RRAM devices, among the most promising systems are HfO₂ RRAM metal-insulator-metal (MIM) based devices. Previous investigations have proposed that the conduction mechanism in these devices is derived from filamentary conduction paths within the transition-metal-oxide [18, 20, 21]. One widely accepted explanation is the migration of oxygen vacancies within the transition-metal-oxide insulator. These defects would then form the conducting filament in the RRAM device [18, 20, 21]. However, to the best of our knowledge, no direct atomic scale experimental evidence establishes this transport mechanism. Electrically detected magnetic resonance (EDMR) measurements could provide such evidence.

Oxide-based RRAM devices typically involve metal-oxide dielectrics grown via atomic layer deposition on a lithographically placed bottom contact. An oxygen scavenging layer is generally deposited above the oxide before depositing a top metal contact to complete the RRAM device. The virgin device is “formed” via current controlled voltage pulses, forming the current path. By sweeping the voltage polarity the device can be “switched” from the low-resistive state (LRS) to the high-resistive state (HRS). This is the basis of the memory cell. The I-V response is typically a hysteresis curve which is current limited at the extremes. This allows for slow voltage-swept switching between LRS and HRS. Another method for switching is pulsed-program-verify switching. This method, which has been utilized on these devices, drives a voltage pulse for a very short period of time (~10 ps – 100 ns) across the RRAM device [22], [23]. The resistance is measured in between pulses, and the memory state can be homed in to achieve 10x to 100x difference in SET/RESET state. These small devices can be easily incorporated into CMOS design, allowing for seamless memory storage.

RRAM has great potential for outer space applications due to its scaling density, limited power consumption, and long-term endurance. Currently, there is no high-density non-volatile memory (NVM) option for outer space applications that is resistant to high levels of radiation damage. (FLASH memory is limited to a total ionizing dose (TID) hardness of ~75krad (Si) [7].) Recent work suggests a potential limit for TID in HfO₂ RRAM devices. Fang *et al.* utilized X-ray photoelectron spectroscopy (XPS) and electrical measurements to identify a TID limit of ~5.2Mrad [19]. Their work indicated a weakening of the conductive filament within the oxide in devices subjected to this (5.2Mrad) total dose. Below this level, there was almost no change in the measured characteristics. (Small shift in SET voltage, but no change in resistance). Their explanation for the increase in oxygen vacancies measured at the surface was to link the process to radiation induced “broken Hf-O bonds” which were measured via XPS as an increase in

“nonbridging oxygen”. Other groups tested the C-V response, switching characteristics, and filament stability after gamma [19][24][25] and even proton-radiation [26] finding similar, if not better, resistance to radiation. Although these studies provide real insight, at the present time, there is effectively no direct evidence for the physical and chemical nature of the electrically active atomic scale defects involved in the radiation damage mechanisms in the leading candidate systems involving HfO_2 .

The EDMR technique called spin dependent trap assisted tunneling (SDTAT) is relatively new; it can identify defect sites within the band gap of an insulator [10][17][27]. If a defect is identified via SDTAT within an oxide-based RRAM cell, that defect must be involved in device transport.

Previous conventional EPR experiments have analyzed the impact of gamma-irradiation on 30 nm HfO_2 -films grown via atomic layer deposition (ALD) on a thin film of SiO_2 . Ryan *et al.* [28] identified two atomic scale defects directly caused by gamma-irradiation in their gate-stack films: an O_2^- coupled to a hafnium ion and an HfO_2 oxygen vacancy center. Some results of the Ryan *et al.* study are shown in Fig. 24. Figure 24 (a) shows the full EPR response obtained after gamma-irradiation. This response involves two spectra. On the left side of the figure the spectrum due to the O_2^- center is illustrated. This defect involves an O_2^- coupled to a hafnium ion. The spectrum is linked to the three labeled g tensor components. Fig. 24 (b) is a WINEPR SimFonia simulation of the same O_2^- center. The experimental results are reasonably consistent with the simulated spectrum. Such spectra have been convincingly linked to O_2^- centers in multiple systems in the past [29]. A schematic diagram of such a defect is shown in Fig. 24 (c) (The unlabeled spectrum on the right side in Fig. 24 (a) has been attributed to the oxygen vacancy center).

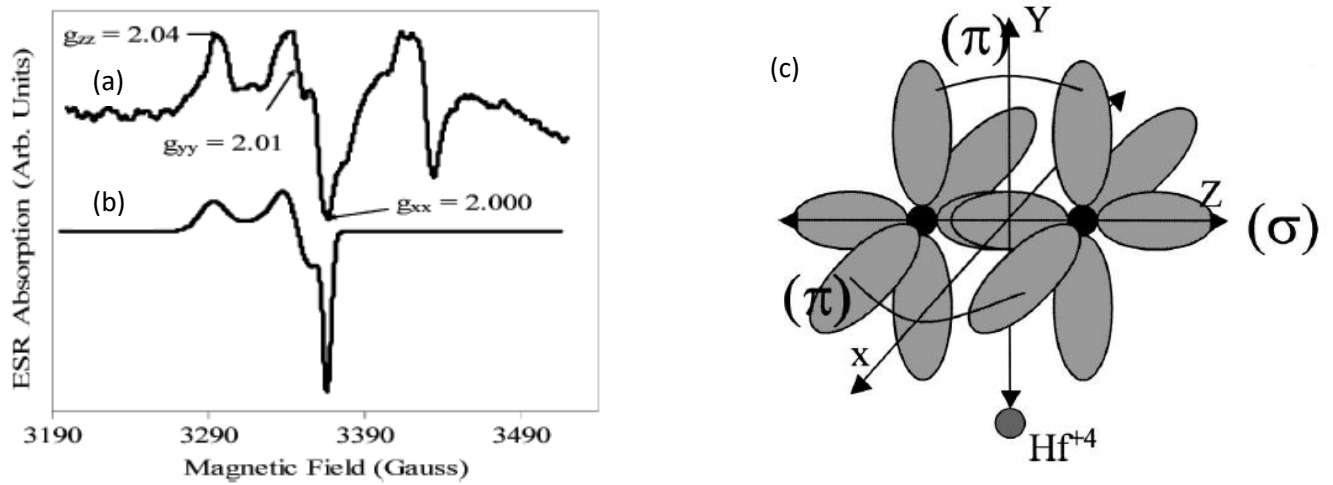


Figure. 24. Illustrates (a) EPR spectrum of HfO_2 -films post gamma-irradiation and (b) (pictured below (a)) is a simulation of an O_2^- molecule defect coupled to a hafnium ion (c) Schematic diagram for an O_2^- molecule defect.

Kanzig and Cohen have developed a model relating this EPR spectrum to the O_2^- center [29-31]. It is widely accepted in the literature for many metal oxides [30][31]. Their model is based upon the electronic ground-state energy levels for the O_2^- in an ionic system, shown in Fig. 2 (c). Since the Hf-O bond has a 70% ionic character, this model works for the HfO₂ system. The crystal field around the defect eliminates the degeneracy of the π bonding and antibonding levels, splitting the $2p\pi_g$ orbitals by an energy Δ , shown in Fig. 3. Equations (10) – (12) identify the expressions for the three g tensors associated with the O_2^- center [29]:

$$g_{xx} = g_e \left(\frac{\Delta^2}{\lambda^2 + \Delta^2} \right)^{\frac{1}{2}} - \frac{\lambda}{E} \left[- \left(\frac{\lambda^2}{\lambda^2 + \Delta^2} \right)^{\frac{1}{2}} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{\frac{1}{2}}} + 1 \right] \quad (10)$$

$$g_{yy} = g_e \left(\frac{\Delta^2}{\lambda^2 + \Delta^2} \right)^{\frac{1}{2}} - \frac{\lambda}{E} \left[- \left(\frac{\lambda^2}{\lambda^2 + \Delta^2} \right)^{\frac{1}{2}} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{\frac{1}{2}}} - 1 \right] \quad (11)$$

$$g_{zz} = g_e + 2 \left(\frac{\lambda^2}{\lambda^2 + \Delta^2} \right)^{\frac{1}{2}} l, \quad (12)$$

where $g_e = 2.00232 (\dots)$ is the free electron g value, and λ is the spin-orbit coupling of oxygen (usually taken to be 0.014). The energy level separations, E and Δ , are illustrated in Fig. 25. The l parameter is the correction to the angular momentum about z caused by the crystal field and is normally close to one. Typically, $\lambda < \Delta \ll E$, and therefore to a first order approximation we may simplify (2)-(4) as: $g_{xx} \cong g_e$, $g_{yy} \cong g_e + 2\lambda/E$, and $g_{zz} \cong g_e + 2\lambda/\Delta$. Therefore, g_{xx} is typically near the free electron $g_e = 2.00232(\dots)$, and g_{yy} is usually shifted to a somewhat higher g -value. Depending on this local environment, and therefore the crystal field splitting Δ , the value of g_{zz} could be significantly shifted from the free electron value [13], [29]. If only modest short-range order exists in the immediate vicinity of the defect sites, one would anticipate the powder pattern spectrum observed by Ryan *et al.* In a more highly ordered system, the simulation in Fig. 24 (b) would be anticipated. However, inspection of (10) (11) and (12) indicates that this characteristic line shape could be greatly broadened if significant site to site differences existed among these defects. The difference between defect sites with moderate short- range order and very highly disordered sites is illustrated in Fig. 26 (a) and (b), respectively. The net effect of the increased disorder is to greatly broaden the left side of the EDMR spectrum, with considerably less broadening of the component of the trace on the right corresponding to a $g \approx 2.000$.

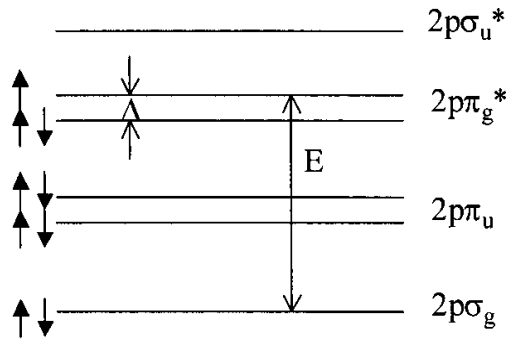


Figure 25. Electronic energy levels of the O_2^- defect, with E and Δ as the energy level separations.

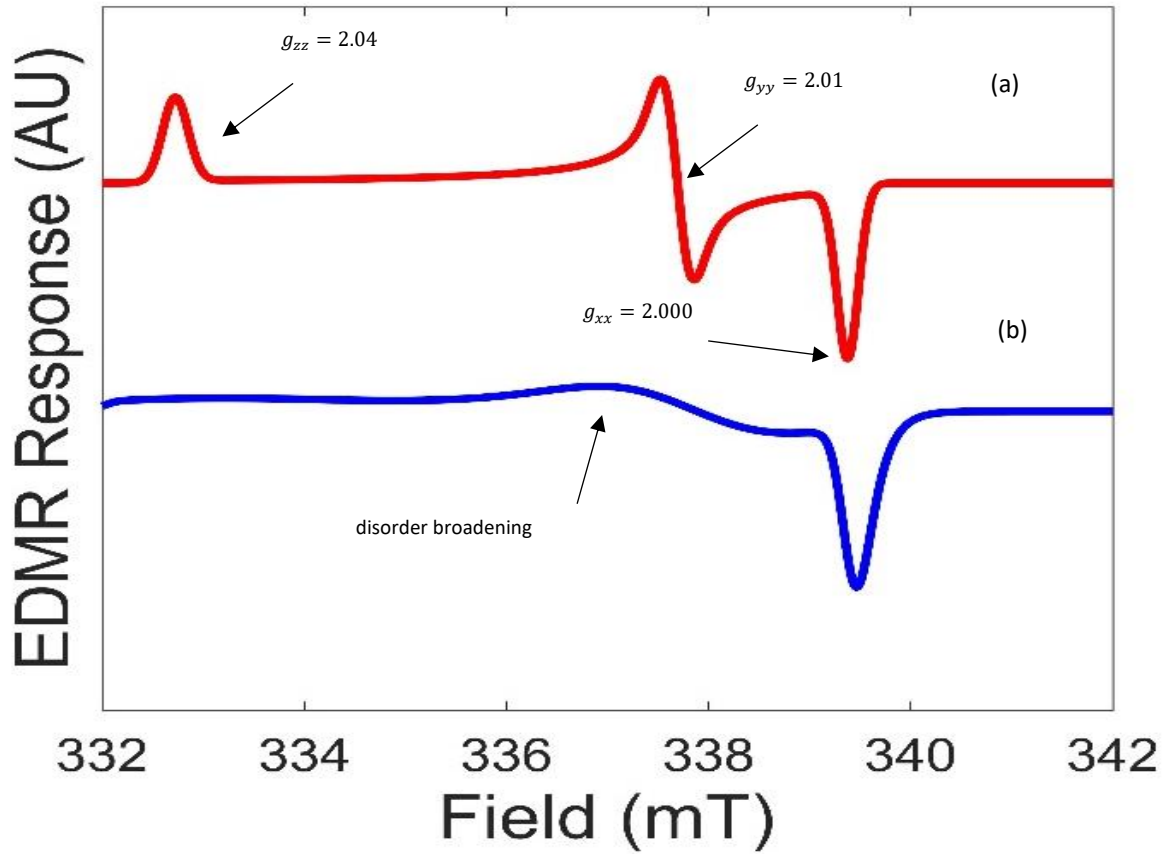


Figure 26. (a) EDMR spectra simulated via *EasySpin* software with $g_{xx} = 2.000$, $g_{yy} = 2.01$, and $g_{zz} = 2.04$ without any line broadening. (b) The same g tensor components with significant broadening due to disorder near the defect.

In this study, we utilized TiN/Ti/HfO₂/TiN RRAM memory cells with a 5 nm Ti layer acting as the oxygen scavenging layer. The memory cell was mounted to a printed circuit-board (PCB) and electrical connections were made via wire bonds, thus excluding periphery logic. This entire apparatus is small enough to fit inside the microwave cavity. These RRAM devices were cycled via the pulse-program-verified switching technique [5]-[6]. These devices were cycled by Nminibapiel *et al*, and their switching results are reported elsewhere [22][23]. EDMR was then performed on the cycled devices. After EDMR measurements, the cycled devices were subjected to 1 Mrad, and subsequently 10 Mrad of ⁶⁰Co gamma-radiation. EDMR was again performed after each radiation dose. These 200 nm by 200 nm devices are cross-point type RRAM with 5.8 nm thick HfO₂ deposited via atomic layer deposition. Additional details about the device structure has been reported elsewhere [32]. For all EDMR measurements we utilized an EDMR spectrometer with a Lakeshore magnet, Mirco-Now microwave-bridge, Stanford Preamplifier, and LabView data acquisition software. We have made EDMR measurements with identical biasing conditions and spectrometer settings before and after each period of gamma-irradiation. We have also

measured the resistance of these devices before and after gamma-irradiation. These measurements were made directly across the memory cell of the RRAM device, bypassing the other RRAM circuitry by wire bonding directly to the memory cell. We also investigated the EDMR position of the center line versus lock-in phase.

EDMR measurements on an LRS HfO₂ RRAM device and on an HRS HfO₂ RRAM device were made before and after 1Mrad of ⁶⁰Co gamma-irradiation. The responses are shown in Fig. 27 (a) and (b) respectively. Before gamma-irradiation, the measured DC resistances were 10k Ω for the LRS and 1.41M Ω for the HRS. The HRS and LRS devices exhibited no EDMR response before gamma-irradiation, as shown in Fig. 27 (a) and (b).

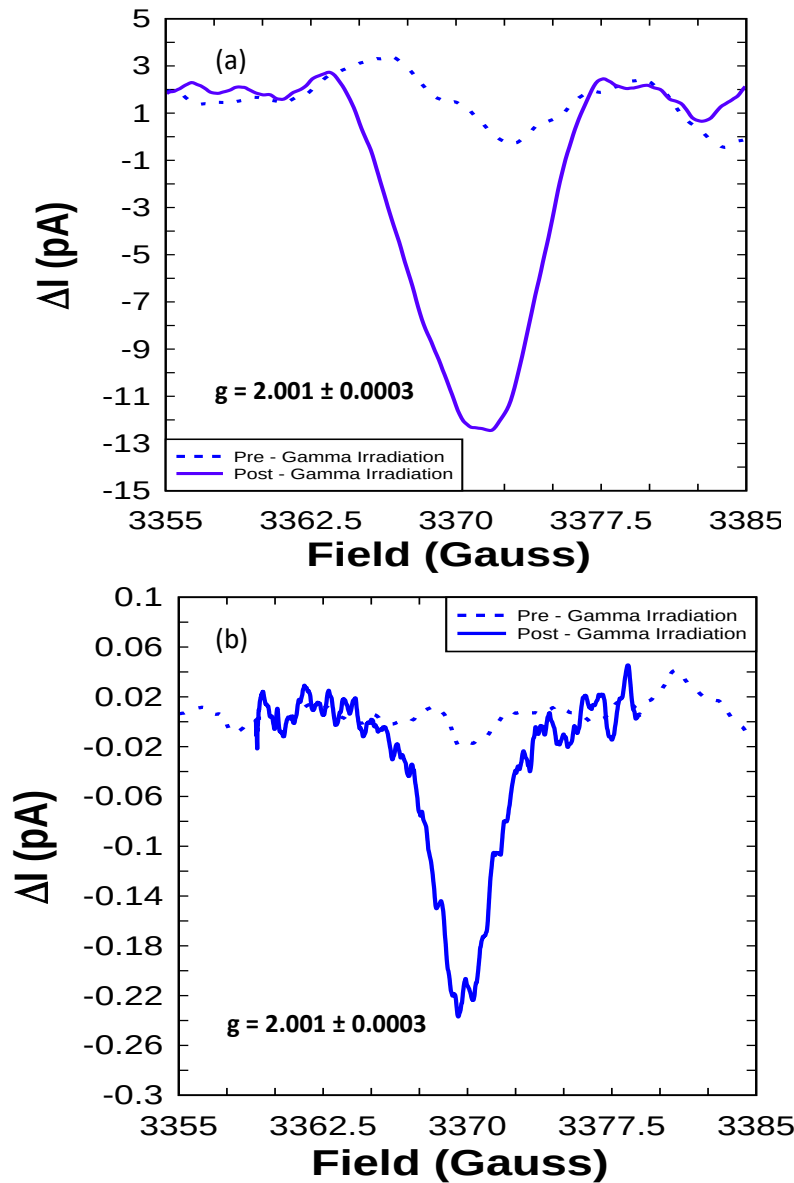


Fig. 27. EDMR response (in picoamperes (pA)) of both the (a) LRS device and (b) the HRS device before and after irradiation of the samples.

After gamma-irradiation, the measured resistances were effectively unchanged ($\sim 1\%$). Any small change in the resistance may have been the result of relaxation within the RRAM device. However, even without a significant change in resistance, we do measure a large increase in the EDMR response with a zero-crossing g of 2.001 ± 0.0003 . This response was measured with a constant applied voltage of 160 mV for the LRS, and 5 V for the HRS. The change in current due to TAT is 80 pA for the LRS and 0.22 pA for the HRS. Although the g value and line shapes were approximately the same, the amplitude of the EDMR is strongly dependent upon the resistance state; it is approximately five parts per million change in current for the LRS and approximately one part per billion change in the HRS current. The EDMR response is relatively small, but the radiation induced change in the resistance state is also relatively small; no more than about one percent. The relatively small EDMR response is not surprising.

This response is also independent of orientation within the magnetic field (shown in Fig. 28 (a) and (b)); the defect g -tensor is isotropic.

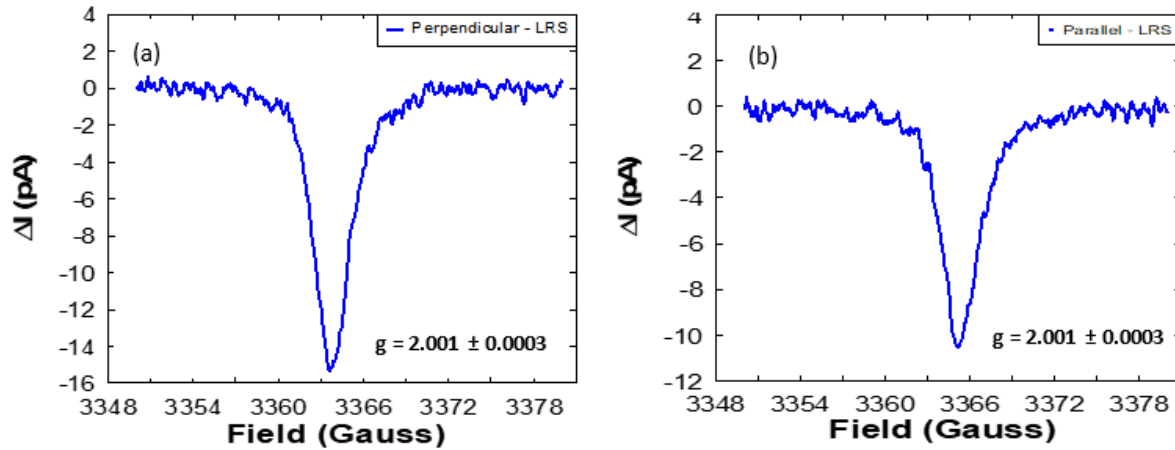


Fig. 28. EDMR response of the LRS device with the device surface (a) perpendicular to the B_0 field and (b) parallel to the B_0 field after gamma irradiation. The response yields the same g -value regardless of orientation.

In a series of measurements, we maximized the EDMR response as a function of lock-in phase. In no case were we able to completely eliminate the out of phase signal. Depending on the lock-in phase, the response exhibited a dual-peak response. This multiple line spectrum suggests the presence of multiple mechanisms in the EDMR.

A follow up dose of 10Mrad of ^{60}Co gamma-irradiation was applied to the same devices. The measured resistances remained unchanged after irradiation. EDMR was again performed on these devices in a comparison measurement. This comparison of 1Mrad versus 10Mrad is shown in Fig. 29. After the second dose, a significant increase in the EDMR response is measured. This shows that the gamma-irradiation has a significant impact on the defect structure within the RRAM memory cell.

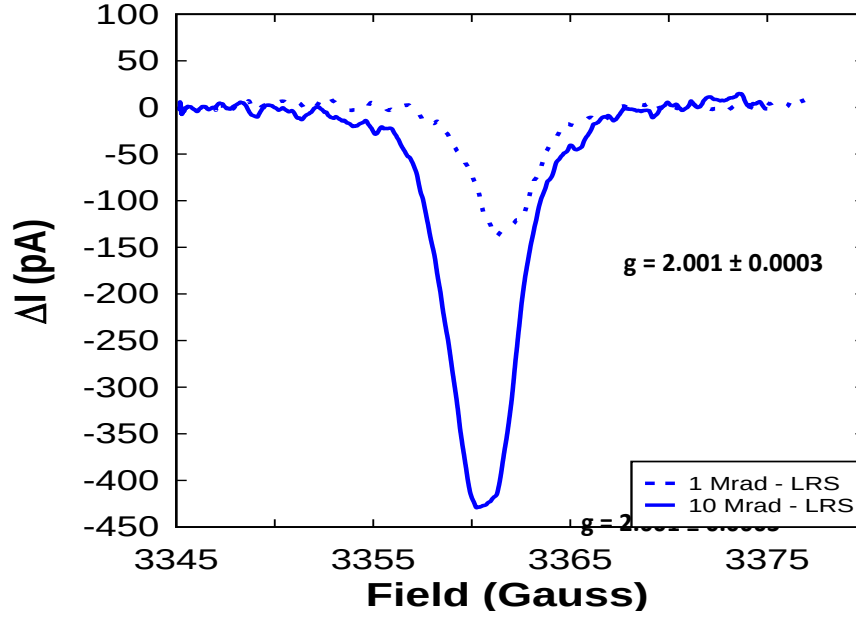


Fig. 29. EDMR comparison of the LRS after 1 Mrad of irradiation and 10 Mrad of irradiation. At the same EDMR settings, a significant increase in the EDMR response is measured after 10 Mrad of irradiation.

In order to determine the identity of this defect responsible for the EDMR response, it is useful to compare a wider EDMR sweep of the RRAM device to the Ryan *et al.* HfO₂-gate-stack-film based EPR response illustrated in Fig. 24 (a). As discussed previously, these observed peaks in Fig. 24 (a) represent the g tensor components of the O_2^- coupled hafnium ion. If the local environments of the defects are more or less the same, one would anticipate an O_2^- spectrum similar to that of Fig. 25 (a) and Fig. 25 (b). However, if the local sites are highly disordered, one would expect the g_{zz} and g_{yy} components to be broadened possibly to the point where they would be no longer observable; however, a relatively sharp component corresponding to $g_{xx} \approx 2.000$ would remain. A wider EDMR sweep of the RRAM device does not yield any other peaks. Therefore our results are reasonably consistent with what would be expected in the highly disordered case, in which the broadening would produce a single line with $g \approx 2.000$.

These results suggest that the O_2^- defects, which are created during radiation, are directly involved in electronic transport in HfO₂ RRAM devices. We believe this is the first atomic scale identification of a defect directly involved in transport within oxide-based RRAM. Surprisingly, we do not see any direct evidence for oxygen vacancy centers in electronic transport. The work of Shluger *et al.* [33], Robertson *et al.* [15], and others [36], [37] indicate that both defects exhibit multiple levels in the HfO₂ bandgap and are thus reasonable candidates for filamentary transport. It should be noted that, as others have previously reported, only very small changes occur in the electronic behavior of these devices subjected to rather high levels of ionizing radiation. The results thus also are consistent with the idea that these devices could be quite radiation hard.

Conclusion with regard to the RRAM Devices:

We show that EDMR measurements can detect radiation induced defects which are clearly involved in electronic transport in TiN/Ti/HfO₂/TiN RRAM devices. To the best of our knowledge, these results provide the first direct atomic scale evidence for defect centers involved in any form of RRAM transport. A strong resonance peak was observed with a zero-crossing g of 2.001 ± 0.0003 . This spectrum is consistent with an O_2^- center within the HfO₂ [12]-[13], with significant broadening of the g_{zz} and g_{yy} g -tensor components due to disorder within the defect environment. These results may be useful for understanding radiation effects in other RRAM devices with similar material systems. That is, one might expect similar defect centers to be involved in transport in other RRAM systems based on similar metal-oxide chemistry. Surprisingly, the response appears to be inconsistent with the expected spectrum due to oxygen vacancies. Our electrical measurements of gamma-radiation on HfO₂ RRAM devices are generally consistent with those reported by others, but we believe the local environment of the O_2^- center is affecting the line shape. After radiation there was no significant change in the resistance. However, it is important to note that we did measure a significant change in the EDMR response. This means the gamma-radiation does change the structure of some defect centers that are directly involved in electronic transport. This change in the defect centers will affect the device performance. However, this change is so small relative to conventional SET/RESET resistances that these RRAM devices are effectively radiation-hard at these levels.

III d Silicon -Germanium based Metal Oxide Silicon Field Effect Transistors

There is considerable interest in silicon germanium based MOS technology [38-40]. This is so because it is possible to make reasonably high quality SiGe/oxide interfaces and the effective channel mobility of transistors based upon these interfaces can be higher than is the case for devices based upon silicon/oxide interfaces. We have explored SiGe based MOSFETs utilizing charge pumping (CP), spin dependent charge pumping (SDCP) and gated diode, so called DCIV, electrically detected magnetic resonance (EDMR) as well as near zero field magnetoresistance (NZFMR). The measurements were made on Si_{0.6}Ge_{0.4} alloy planar p-MOSFETs provided by an industrial R and D laboratory. The hafnium-based high-k gate stacks had an effective oxide thickness of 12 Angstroms. Samples were studied with gate lengths from 2 μ m-10 μ m and gate widths from 20 μ m-100 μ m. The SiGe transistors were made from epitaxially grown Si_{0.6}Ge_{0.4} on Si.

It should be mentioned at the outset that our SiGe studies met with what might be charitably characterized as a mixed level of success. We made multiple attempts to improve the signal to noise level in these EDMR studies. In most cases, we were unable to achieve an EDMR response above our detection limits. However, in a few cases, we were able to observe EDMR responses and these limited data suggest the underlying physical problem, as well as strong evidence for the chemical nature of the interface traps in these devices. This will be discussed later.

Samples were mounted onto specially made PCB sample mounts, essentially the same as those utilized in the other systems investigated, to hold the devices in the EDMR/NZFMR spectrometers. Electrical contact to the body of the MOSFETs was made using silver paint and electrical contact to the testing pad of the MOSFETs was made via wire bonds. The SiGe MOSFET samples were irradiated up to 500kRad using a Cobalt-60 gamma dry cell irradiator located at the Penn State Radiation Science and Engineering Center. Samples were biased during irradiation.

The electrical characteristics of the MOSFETs changed only slightly due to irradiation. The drain current vs gate bias is shown below for the pre-radiation and post-radiation samples in Figure 30. The transconductance of the MOSFETs decreases after irradiation.

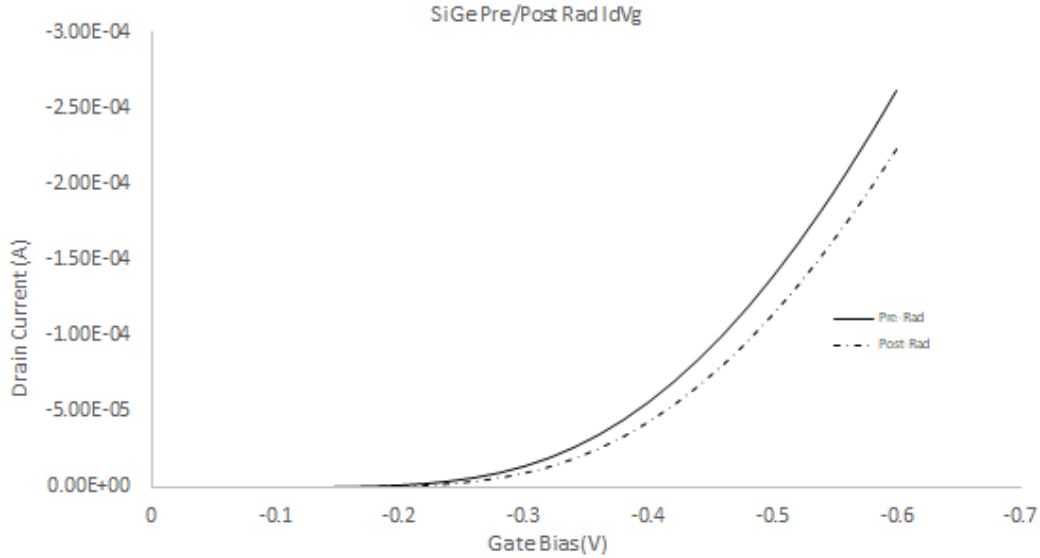


Figure 30. Drain current vs gate bias in $\text{Si}_{0.6}\text{Ge}_{0.4}$ alloy p-MOSFET before and after irradiation. A threshold voltage of approximately -0.25V was extracted using these measurements.

Charge pumping measurements were made on the SiGe MOSFETs using the constant low (of -0.5V to achieve strong inversion) technique. Due to high levels of gate leakage, CP measurements were made at two different frequencies, 100kHz and 1MHz. A constant shape factor (ratio of high time to rise time) of 4 was used to ensure that the gate leakage was the same for both frequencies. The CP curves below were made by subtracting the low frequency from the high frequency measurement, effectively removing the effects of gate leakage from the measurement. Results are shown in Figure 31. It is clear that the maximum CP current is greater for the irradiated sample, indicating that interface states are created during irradiation. The total interface state density increased by approximately 30% due to irradiation of 500 kRad.

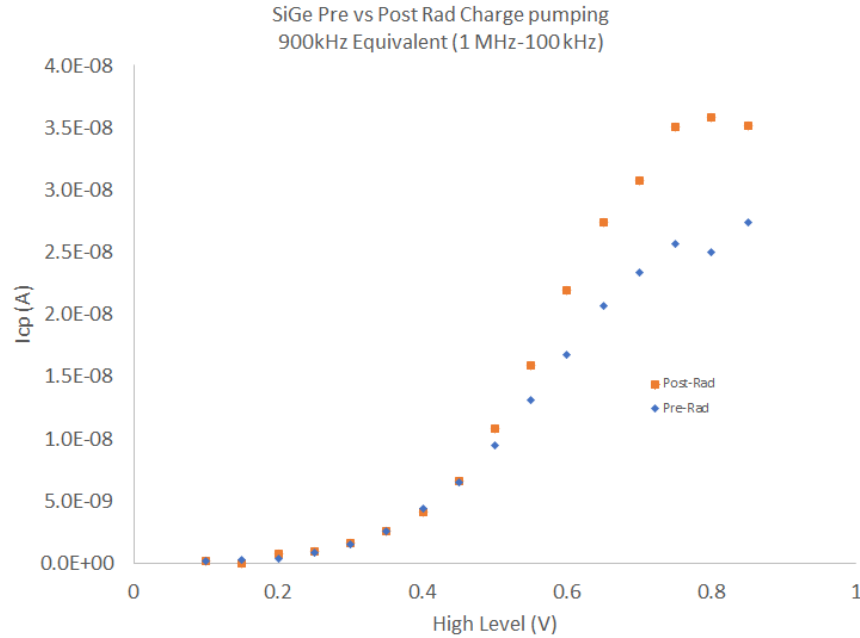


Figure 31. Constant low charge pumping measurement for $\text{Si}_{0.6}\text{Ge}_{0.4}$ alloy p-MOSFET. Values of I_{cp} given by the difference between the current at 1MHz and 100kHz.

This CP measurement indicates that the flat-band voltage occurs at approximately +0.8V, therefore for SDCP measurements, a 1MHz waveform with a low level of -0.4 and high value of 1.2V was chosen. CP measurements were performed on SiGe MOSFETs in a low-field EDMR/NZFMR spectrometer to perform SDCP measurements. Representative pre- and post- irradiation low field spectra are shown in Figure 32. The EDMR amplitudes increased modestly with irradiation, a result qualitatively consistent with the modest observed increase in interface trap density. It is curious to note that the EDMR signal is phase shifted with respect to the NZFMR signal, that is the EDMR signal has an up-down-up shape while the NZFMR signal has a down-up-down shape. The “up-down” shape of the EDMR traces indicates that the EDMR response corresponds to a resonance induced increase in CP current whereas the “down-up” response of the pre irradiation curve corresponds to a (puzzling) decrease in CP currents. At the present time we simply have this result but cannot offer a plausible explanation. The NZFMR measurements were not a topic of this investigation but are an almost unavoidable result of the low field EDMR.

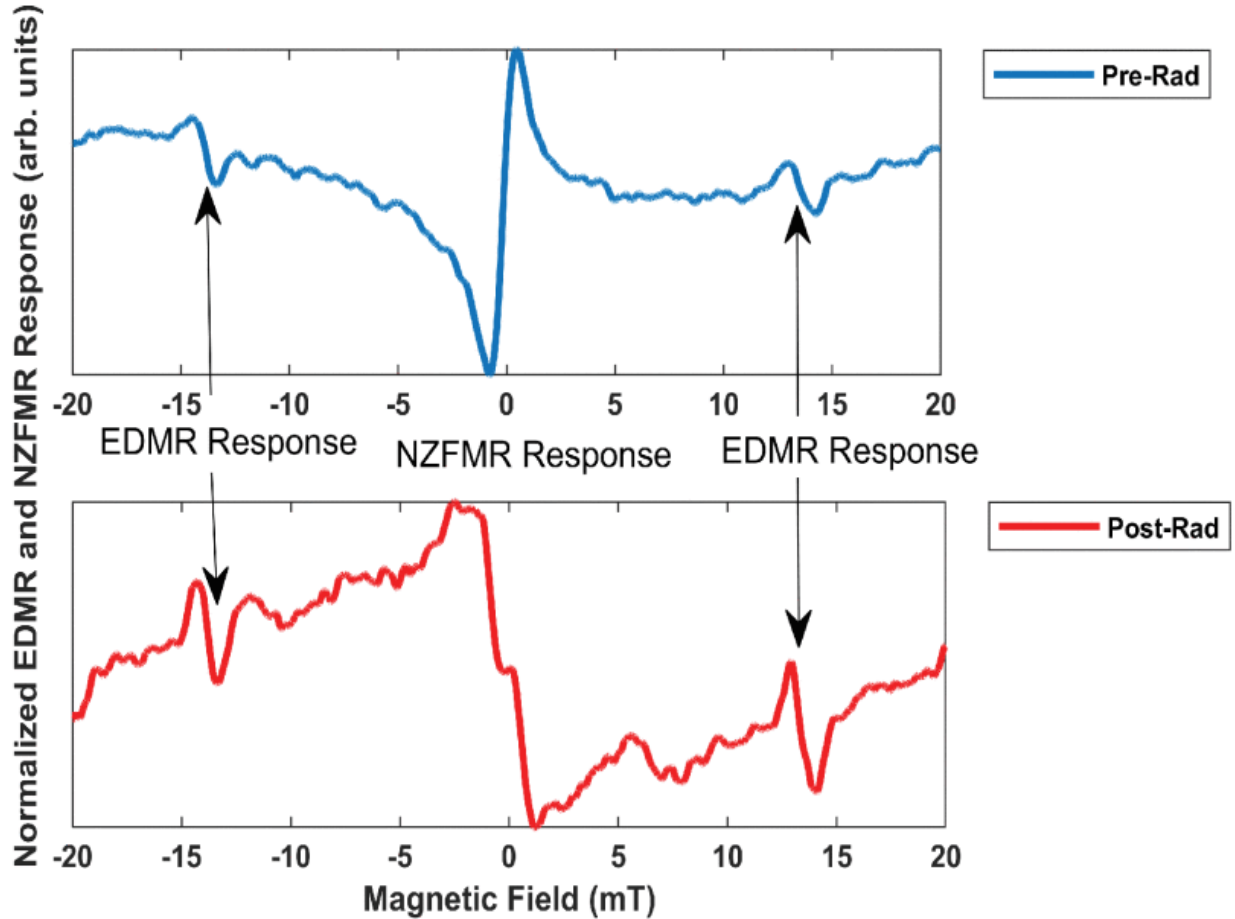


Figure 32. Low field and frequency (365 MHz) EDMR and NZFMR response for lateral SiGe MOSFETs for pre-irradiation (top blue) and post-irradiation (bottom red) utilizing SDCP. The charge-pumping frequency was 1 MHz and the pulse height used was 1.6 Vpp. The modulation amplitude was 1 milliTesla. The RF source output power used was approximately 40 mW.

Additional EDMR results are shown in Fig. 33. In this figure, the spectra are normalized to illustrate modest differences in the pre- and post- irradiation SDCP EDMR line shapes. Also note that, in figure 33, with the measurements involving a lower detection frequency and field, the signal to noise ratio is higher than in figure 32. It is difficult to draw any definitive conclusion from such a comparison, but it is worth noting that all our attempts at very high field and frequency, about 0.340 Tesla and about 9.5GHz, failed to detect any EDMR response.

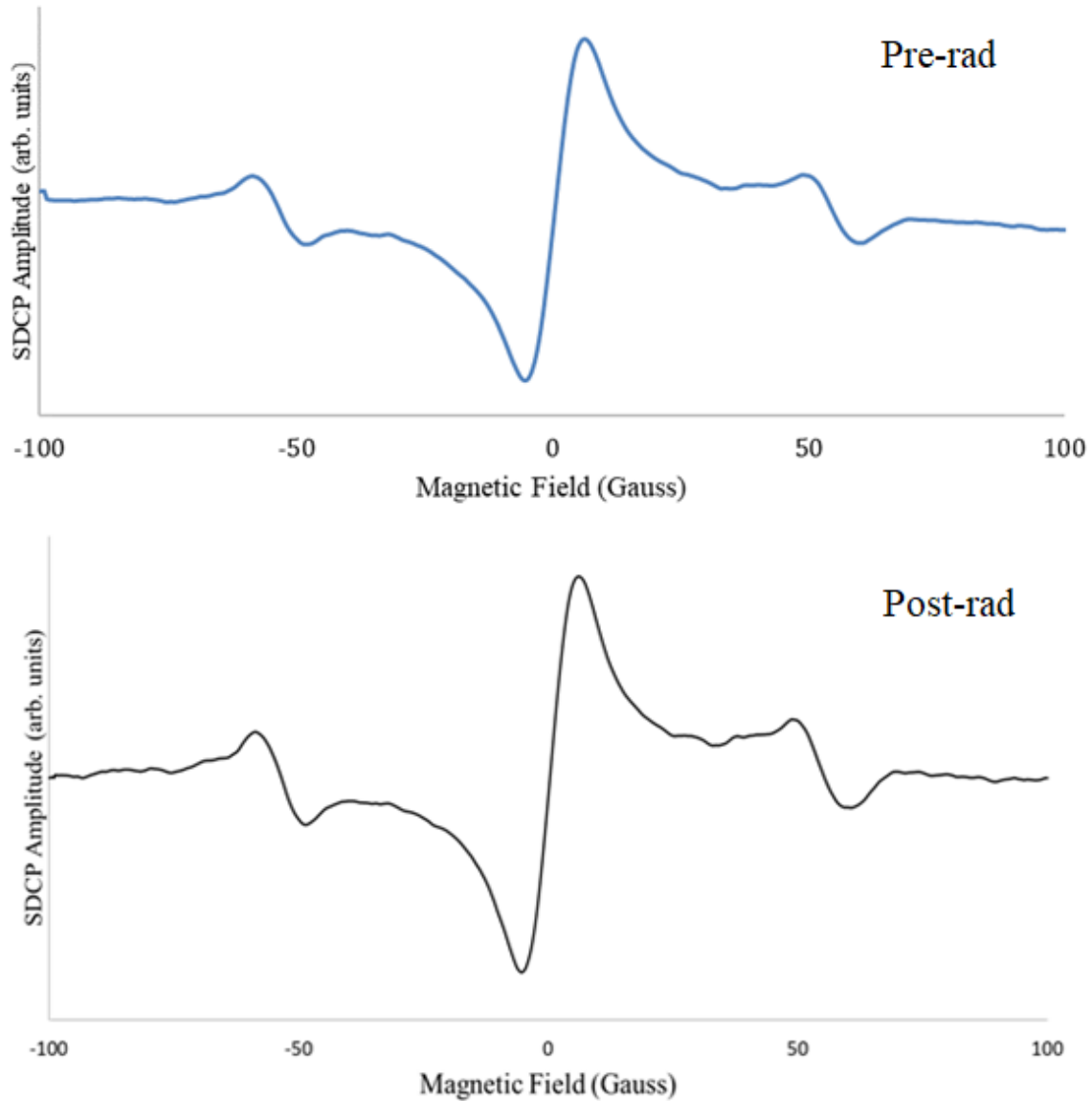


Figure 33. Near zero field magnetoresistance and low field EDMR (151MHz) SDCP in pre-irradiated (blue, top) and post-irradiated (black, bottom) $\text{Si}_{0.6}\text{Ge}_{0.4}$ alloy p-MOSFET. The EDMR signal is 11 Gauss wide while the NZFMR signal is 15 Gauss wide.

A disappointing but informative aspect of the SiGe MOSFET EDMR studies was our total inability to observe EDMR at high magnetic fields, that is, at frequencies of approximately 9.5 GHz and fields of about 0.340 Tesla. Although we made measurements with signal, averaging of up to five

days and with essentially all plausible spectrometer settings, we were unable to detect reproduceable spectra. At low fields and frequencies, as discussed, we were able to observe fairly high signal to noise spectra. As we have discussed previously in this report, contributions to the EDMR (and classical EPR) line widths due to the range of g -tensor components scale with the field. In our other studies, we observe quite dramatic differences in linewidth versus field. There is only one obvious reason for our inability to observe EDMR spectra in the SiGe samples at high field and that is clearly that the breadth of g -tensor components in these spectra are much greater than would be the case in our other observations.

Conclusions with regard to SiGe

This result provides strong evidence that the interface trap defects in the SiGe devices are not primarily silicon dangling bonds and are quite probably germanium dangling bonds, or at least defects in which germanium atoms play a large role. We know this because Ge nuclei have 32 protons whereas silicon nuclei have 16 protons. The spin orbit coupling induced changes in g , all things being equal, is a strongly increasing function of increasing nuclear charge [4-6].

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Appendix:

Ph.D. Thesis of Colin McKay

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The Pennsylvania State University

The Graduate School

**A NEAR ZERO FIELD MAGNETORESISTANCE STUDY OF SPIN-DEPENDENT
CURRENTS IN SEMICONDUCTOR AND DIELECTRIC MATERIALS**

A Dissertation in

Materials Science and Engineering

by

Colin G. McKay

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of the Requirements
for the Degree of

Doctor of Philosophy

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ABSTRACT

Near zero field magnetoresistance (NZFMR) is a new spin-based spectroscopic technique that offers some of the analytical power of electrically detected magnetic resonance (EDMR) when studying performance limiting defects in semiconductors and dielectrics. NZFMR measurements are far simpler and considerably less complex than other spin-based spectroscopic techniques. NZFMR is based upon the fact that spin-based conductivity of materials can change as an externally applied magnetic field is swept through zero. This results in a spectrum somewhat similar to those observed in electron paramagnetic resonance measurements (EPR). Attempts to interpret this phenomenon are currently being developed. This work focuses on EDMR and NZFMR measurements on three model systems, amorphous hydrogenated carbon (a-C:H), amorphous diamond-like carbon (DLC), and amorphous hydrogenated silicon carbide (a-SiC:H). A major focus of this work is the study of stress induced leakage current (SILC) and time dependent dielectric breakdown (TDDB). These measurements were then used to inform the development of the computational models in order to determine what physical information can be extracted from NZFMR spectra and to provide insight into TDDB. The current in the amorphous thin film samples is primarily due to variable range hopping (VRH) or trap assisted tunneling (TAT). The amorphous carbon samples (both a-C:H and DLC) exhibited unstable electrical characteristics under constant biasing conditions over time. This suggests that there are physical changes occurring in these samples over time. The a-C:H samples exhibit a behavior indicative of TDDB with a decrease in current over time along with a reduction in EDMR and NZFMR signals and trapped space charge. The DLC shows an increase in current due to stress along with a change in the shape of the EDMR and NZFMR signals, likely indicating the introduction of new defects. Some low field EDMR and NZFMR results are also reported in

SiGe alloy p-MOSFETs. A new NZFMR spectrometer was built into a wafer probing station to allow for non-destructive measurements to be made on larger samples, rather than dicing wafers and mounting samples to custom made holders, allowing for a higher throughput of EDMR and NZFMR measurements.

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Chapter 1

Introduction

Near zero field magneto-resistance (NZFMR) is a new spin based spectroscopic technique that may offer much of the analytical power of electrically detected magnetic resonance (EDMR). This technique is simpler and more cost effective than EDMR and may be utilized to study electrically active point defects in a wide variety of semiconductor and dielectric materials that may contribute to reliability problems such as stress induced leakage currents (SILC) and time dependent dielectric breakdown (TDDB). NZFMR also offers the opportunity to study three-dimensional device architectures that block the microwave or radio frequency radiation required for EDMR. The theoretical aspects of NZFMR are only starting to be understood as new computational models are being developed to analyze NZFMR spectra. Well-developed computational models would allow for the extraction of certain physical parameters related to the defects in the material such as hyperfine coupling constants and site to site hopping rates, as well as dissociation rates in a wide variety of material systems.

Several model systems, amorphous carbon and amorphous silicon carbide, were studied in order to learn about the electronic transport as well as SILC and TDDB processes in the materials. Comparisons to a relatively crude and newly developed NZFMR computational model allowed for the extraction of reasonable values for the parameters discussed previously given the limitations of the models and the compositions of the samples. The parameters involved in the model, such as hopping and dissociation rates, have been linked to physical phenomena involved in transport in the structures. This work shows that a relatively crude model, based upon the stochastic quantum Liouville equation (SLE) can generate NZFMR simulations in fairly close agreement with the observed NZFMR spectra. The rudimentary SLE

model results are in reasonable agreement with the observed NZFMR spectra. The results of this study will inform further development of the computational NZFMR models in order to analyze other systems.

Chapter 1.1 Reliability Problems; Variable Range Hopping, Stress Induced Leakage Currents, and Time Dependent Dielectric Breakdown in Semiconductors

Variable range hopping (VRH) [1], [2], also known as trap assisted tunneling (TAT), is a phenomenon in which a dielectric or semiconductor material has a high enough defect density to allow for electronic transport through the dielectric or semiconductor via site to site tunneling. Electrons and/or holes tunnel through the dielectric or semiconductor from site to site until reaching the other side. Dielectric and insulator materials are typically utilized to prevent the flow of charge carriers across them, so a large hopping current can severely inhibit the performance of a device in which they are a part. The band diagram of such a material and the transport path through it can be idealized to look like Figure 1.1 below.

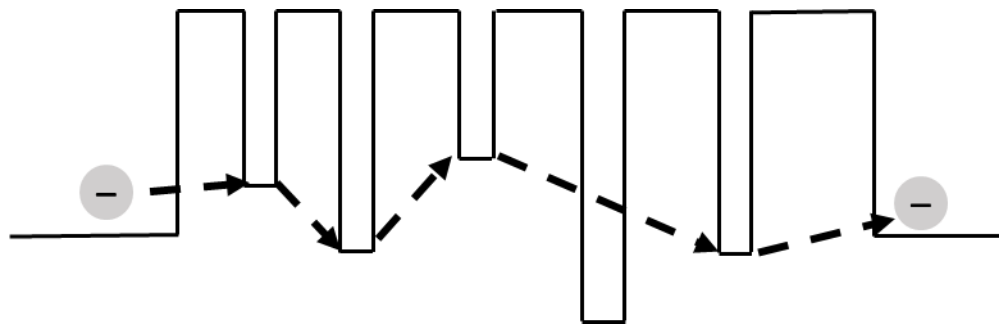


Figure 1.1: Idealized band diagram of potential wells (traps) in a dielectric which allow charge carriers to tunnel from site to site. Only defects within certain energy levels of the electron can be accessed.

VRH is a tunneling process which depends on the depth and separation of the wells in the band structure as well as upon the temperature. The primary defects of concern are those within approximately $2kT$ of the Fermi level, where k is the Boltzmann constant and T is the absolute temperature. Sites well below that level will have too high a probability of being occupied and sites well above will require the electron to gain too much energy to jump. At low voltages, this process is fairly ohmic and scales with an exponential of the reciprocal of the one-fourth power of the temperature in the early model proposed by Mott that is of the form $\exp(-\frac{A}{T^{\frac{1}{4}}})$, where A is a constant. [1], [2] The $\exp(-\frac{A}{T^{\frac{1}{4}}})$ dependency is not always observed. Efros and Shklovskii [3] have shown that the temperature dependent conductivity scales with $\exp(-\frac{A}{T^{\frac{1}{2}}})$ when accounting for a ‘soft’ gap which arises from the Coulomb interaction between localized electrons.

Thin dielectric materials can begin to degrade under stress if the electric fields in the dielectric approach breakdown causing leakage currents to increase over time. One aspect of this phenomenon is typically referred to as stress induced leakage current (SILC) [4]–[8]; it is one of the primary reliability issues with device scaling as the effect is greater for thinner oxides [5]–[8]. Studies have shown SILC to be caused by an increase in trap assisted tunneling as localized defects are created within the oxide [4]–[7] as well as potentially near the interface [5]. Recent models dictate that inelastic tunneling through the oxide is required to fit the data from SILC experiments [8]–[10]. Most studies agree that trapping defect densities increase with increased tunneling current in a positive feedback loop, making SILC a bigger problem for thinner oxides that are more susceptible to tunneling in the first place. [5]–[8]

Another reliability problem in devices with dielectric materials is known as time dependent dielectric breakdown (TDDB), a phenomenon in which dielectric materials operating

at electric fields below their breakdown field will suddenly and catastrophically fail with little to no warning. TDDDB is not fully understood but it is certain that charge carriers tunneling into and out of the dielectric may play a role. This phenomenon has been studied extensively and has been found in a variety of material systems [11]–[15]. A curious aspect of this problem is the frequent observation of an initial reduction in leakage current through the dielectric before the material breaks down and becomes conductive. Devices that undergo TDDDB go through several types of breakdown during stressing, soft and hard breakdown.[15] In soft breakdown, leakage through the oxide increases slightly and somewhat erratically; in hard breakdown the insulating material essentially becomes conductive [15].

There are several widely utilized models in the literature describing TDDDB. One model for this phenomenon has been known as the “E-model”, because the model predicts that the log of time to failure is linearly proportional to the electric field across the dielectric, as shown in equation 1.1.1. [16]–[18]

$$\ln(TF) \propto \frac{\Delta H_0}{k_B T} - \gamma E_{ox} \quad (1.1.1)$$

where ΔH_0 is the enthalpy of activation for oxide breakdown, E_{ox} is the electric field in the oxide, k_B is Boltzmann’s constant, T is the absolute temperature, and γ is the field acceleration parameter. In this model, the electric field across the oxide generates traps, where overlap between the wave functions of trapped charges eventually create a conduction subband. The increased current and subsequent Joule heating cause the material to break down [17]. A competing theory for the mechanisms involved in TDDDB is known as the “current-based” or “1/E model” [18]–[20]. This model suggests that breakdown is due to hole injection into the oxide and the log of time to failure is proportional to the inverse of the electric field. Recently it

has been proposed that the best explanation of TDDB comes from a combination of both the electric field model and the current-based model [11], [21].

Another potential explanation for TDDB is that electrons tunnel into deep level defects near the oxide/conductor interface, raising the effective barrier height for other electrons attempting to tunnel through, temporarily reducing leakage while simultaneously increasing the electric field in the rest of the oxide. This model provides an explanation for the often-observed initial reduction in dielectric leakage current over time, preceding the eventual catastrophic failure of TDDB. More electrons may continue to tunnel into the dielectric over time, raising the barrier further and increasing the local electric field to levels capable of breaking, for example, Si-O bonds [22].

Chapter 1.2 Electrical Measurements

Many electrically active defects that contribute to these reliability problems in metal-oxide-semiconductor (MOS) devices can be detected using purely electrical measurements. These measurements include, but are not limited to, capacitance measurements [23], [24], the Fitzgerald-Grove gated diode or DCIV measurement [25], and charge pumping [26]–[29]. Capacitance versus voltage measurements on MOS systems can determine the number of interface states and, with assumptions, also determine the amount of oxide charge present in a material by comparing the measured curve to a calculated ideal curve (with no defects). In silicon dioxide on silicon structures, shifts in the curve corresponding to mid-silicon band gap fermi energy are due to oxide charge while interface states cause the curve to stretch [23].

Gated diode direct current versus voltage (DCIV) measurements are fairly simple way to evaluate stressing damage in metal-oxide-semiconductor field effect transistors (MOSFET). In DCIV measurements, the source and drain are forward biased relative to the body and the gate is biased to keep the device in depletion. A recombination current will occur at the interface and will be at a maximum value when the number of electrons and holes are equal, achieved when the quasi-Fermi levels are symmetrically located about the mid-gap at the interface. The increase in current due to recombination provides information regarding the number of interface defects although the method is only sensitive to deep level defects which facilitate recombination [25].

Interface states can also be measured using charge pumping which is sensitive to defects with a wider range of energy levels than DCIV [26]–[29]. In this measurement, the source and drain of a MOSFET are grounded or slightly reversed biased with respect to the channel. Current is measured through the substrate or body as a trapezoidal waveform is applied to the gate to bring the device from accumulation to inversion and back again in quick succession. Interface states are filled and emptied when the Fermi level is swept through the bandgap resulting in a somewhat steady state current through the body due to recombination events at the interface. The recombination current is maximized when the traps are filled and emptied completely each cycle. This occurs when the trapezoidal gate pulse cycles beyond the flat band and threshold voltages. The relationship between the charge pumping current and the defect density when this condition is met is given as [28]:

$$I_{CP}^{max} = qf_{CP}A_{eff}\overline{D_{it}}\Delta E_{CP} \quad (1.2.1)$$

where q is the electric charge, f_{CP} is the frequency at which the gate is switched from accumulation to inversion and back, A_{eff} is the effective gate area, $\overline{D_{it}}$ is the interface trap

density per unit energy, and ΔE_{CP} is the energy window probed by the measurement (typically a large portion of the bandgap). It is important that the time between high and low voltage levels is sufficient to allow free carriers to diffuse away from the interface. In order for equation 1.2.1 to be correct, enough time must also be provided at inversion for the charge carriers to diffuse from the source and drain of the MOSFET to reach and recombine with the trapped charges at the middle of the channel. Both DCIV and charge pumping measurements rely on recombination events which are inherently spin dependent.

Chapter 1.3 Electron Paramagnetic Resonance Family of Measurements

One of the most powerful tools to study defects in semiconductor and dielectric materials is electron paramagnetic resonance (EPR) [30]–[32]. EPR is sensitive to paramagnetic defects in a sample and is used to identify the physical and chemical nature of these defects. The simplest case of a free electron has a well understood magnetic resonance condition; however, an electron's resonance conditions in real materials will deviate from the simplest case mostly due to the effects of spin orbit coupling and electron-nuclear hyperfine interactions [30]–[32]. Spin orbit coupling alters the relationship between the resonance field and the resonance frequency. It can also cause broadening of signals at higher magnetic fields in amorphous and disordered systems. Hyperfine interactions are in effect, the response due to local magnetic fields from nearby magnetic nuclei which cause the measured spectrum of an EPR measurement to be split into two or more lines (or resonance peaks). Broadening of lines due to hyperfine interactions is, to zero order, a constant, independent of resonance field and frequency [33].

Conventional EPR requires a minimum of approximately 10^{10} defects in a sample. Most modern devices have many orders of magnitude fewer defects and, while EPR is sensitive to all

paramagnetic defects, not all defects are electrically active. A different measurement scheme was introduced to get around these limits known as electrically detected magnetic resonance (EDMR) [34], [35]. EDMR measures changes in a sample's current or voltage as defects within it undergoes magnetic resonance.

EDMR requires approximately 10^7 fewer defects in a sample compared to conventional EPR, allowing it to be utilized on fully processed devices, and is only sensitive to electrically active defects, or defects affecting the electrical properties of the device. The size of the EDMR response of a device is also essentially resonant field and frequency independent [35], [36] allowing for measurements to be made across a wide range of resonance fields. This allows one to separate the effects of spin orbit coupling from hyperfine interactions because the effects of spin orbit coupling diminish as the resonance field and frequency are lowered.

There is a response related to EDMR which may be observed as the magnetic field approaches zero [37]–[43]. This is known as the near zero field magnetoresistance (NZFMR) effect. NZFMR measurements are not as complex as EPR or EDMR because they do not require all of the hardware necessary for magnetic resonance. The overall size of the NZFMR signals are often larger than EDMR signals; however, the phenomenon is not yet fully understood. Several studies have measured the NZFMR response in a variety of materials [37]–[42], [44]. The majority of these studies have also utilized resonance measurements in conjunction with the NZFMR measurements. The NZFMR response has also been utilized to as the basis for a high sensitivity, self-calibrating magnetic field sensor [43].

Chapter 2 Electron Paramagnetic Resonance and Electrically Detected Magnetic Resonance

Chapter 2.1 Electron Paramagnetic Resonance

Chapter 2.1.1 Electron Spin

Electrons and some atomic nuclei have an intrinsic angular momentum known as a “spin”. Electrons’ spins are described by the quantum spin vector $\mathbf{S}$, which contains a magnitude and a direction. Electrons’ spins are said to be either ‘up’ or ‘down’, and are described by the quantum number $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$, respectively. This intrinsic spin gives rise to an electron’s magnetic moment

$$\boldsymbol{\mu}_e = g_e \mu_B \mathbf{S} \quad (2.1.1)$$

where $\boldsymbol{\mu}_e$ is the magnetic moment of the electron, g_e is the Landé factor, $g = 2.002319..$ and the Bohr magneton is

$$\mu_B = \frac{|e|\hbar}{4\pi m_e} = 9.27400994 \dots \times 10^{-24} \frac{J}{T} \quad (2.1.2)$$

where e is the electron charge, Planck’s constant $\hbar = 6.626 \times 10^{-34} Js$, and m_e is the electron mass. The electron magnetic moment creates an energy splitting between the spin up and spin down state when the electron spin is placed in an applied magnetic field, $\mathbf{B}$. For the simplest case of an electron otherwise unperturbed by its surroundings, the individual energy levels can be computed from

$$E = -\boldsymbol{\mu}_e \cdot \mathbf{B} = g\mu_B \mathbf{S} \cdot \mathbf{B}. \quad (2.1.3)$$

We choose a reference frame that aligns the magnetic field, $\mathbf{B}$, with the z-axis to simplify the equation to

$$E = -\boldsymbol{\mu}_e \cdot \mathbf{B} = g_e \mu_B S_z B_0 \quad (2.1.4)$$

where S_z is the magnitude of the electron spin vector projected onto the z-axis and B_0 is the strength of the applied magnetic field in the z-axis direction. The magnitude of S_z is either $+\frac{1}{2}$ or $-\frac{1}{2}$ for the spin up and spin down states respectively. The energy difference between these up and down states is therefore described by the equation

$$\Delta E = g_e \mu_B B_0 \quad (2.1.5)$$

and the concept it illustrated in Figure 2.1.

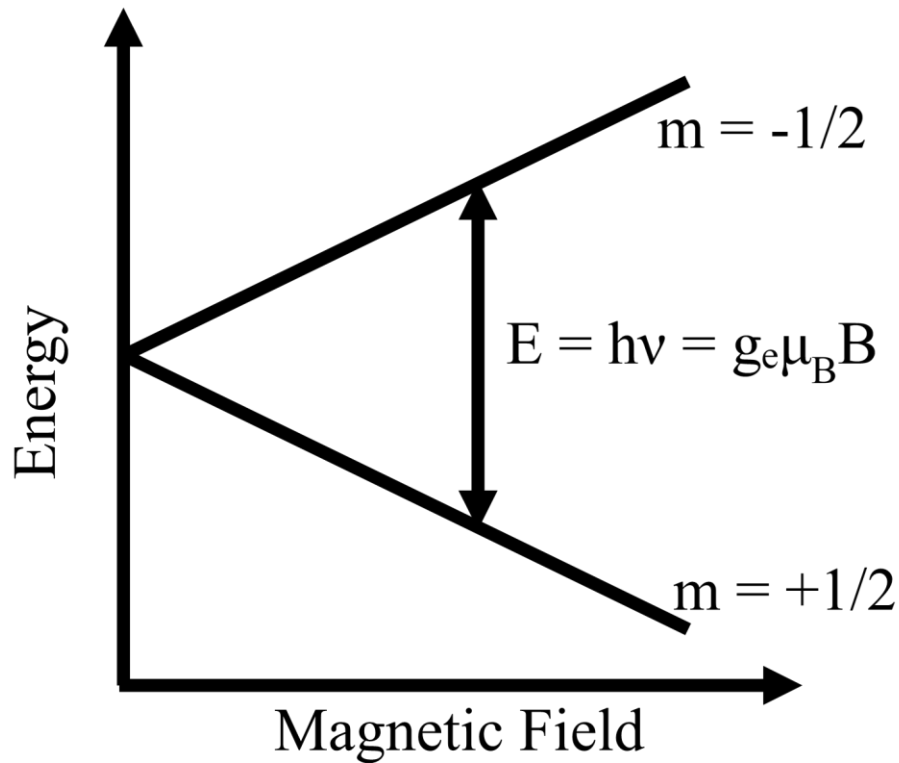


Figure 2.1: Schematic of energy separation between the spin up ($m = +\frac{1}{2}$) and spin down ($m = -\frac{1}{2}$) in an externally applied magnetic field, $\mathbf{B}$. This is typically referred to as Zeeman splitting.

The energy level splitting which occurs when an electron spin is placed in a magnetic field is called the Zeeman effect. The energy splitting is proportional to the applied magnetic field. Electrons in one of these states can absorb or release energy to switch, or ‘flip’, between states. In EPR, this is achieved by exposing the electron spin to electromagnetic radiation. The energy required to flip an isolated electron is described as

$$\Delta E = h\nu = g_e\mu_B B_0 \quad (2.1.6)$$

where h is Planck’s constant and ν is the frequency of the electromagnetic radiation. Equation 2.1.6 describes the simplest case of a free electron isolated from its surroundings, however, unpaired electrons in real materials will deviate from this idealized situation due to their surroundings. Measuring the deviations from this ideal situation gives EPR its analytical power to study the paramagnetic sites in real materials. If no magnetic nuclei are nearby, the EPR condition is given by

$$\Delta E = h\nu = g\mu_B B_0 \quad (2.1.7)$$

where the free electron g from equation 2.1.6 is replaced by an orientation dependent g factor which is best described as a second rank tensor and is one of the tools used to capture deviations from the simplest case of a free electron. More complex expressions can occur under some circumstances not relevant to the work described in this thesis.

In conventional EPR, a sample with paramagnetic centers is placed into a microwave cavity with a very high quality, or Q factor. A standing wave is set up in this cavity to provide an oscillating magnetic field, B_1 , with a frequency of ν . The cavity is placed in a large slowly varying magnetic field, typically provided by an electromagnet which sweeps the applied magnetic field through the resonant field. Resonance is detected when the applied microwave radiation is absorbed by the sample when the resonance condition is met, causing the Q factor of

the cavity to change. This change in Q causes a change in the reflected power back to a diode in the microwave bridge. An absorption spectrum is measured when the reflected microwave power is plotted against the slowly varying magnetic field as seen in Figure 2.2 a). A lock-in detection scheme is utilized to increase the signal to noise ratio by added low frequency modulation coils to the microwave cavity, if the absorption spectrum has a gaussian-like line shape, this results in a derivative like spectrum seen in Figure 2.2 b).

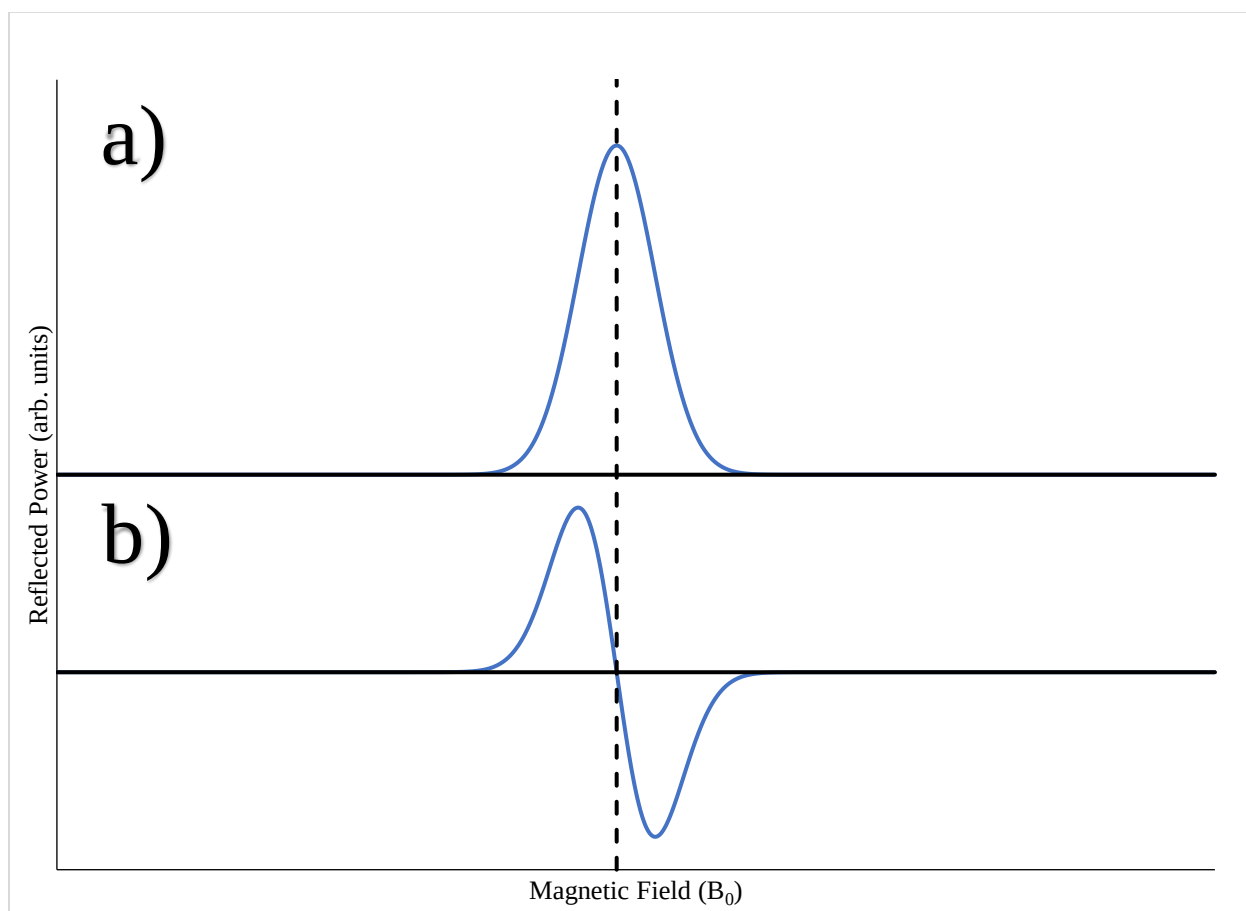


Figure 2.2: a) Simulated EPR absorption response of electron in a paramagnetic center with a fixed microwave frequency and swept magnetic field, B_0 . b) Simulated EPR response using lock-in detection scheme. Modulation and lock-in detection produces an approximate derivative of the absorption response.

It is important to understand how the spins respond to the microwave radiation in the cavity. Electrons in the low energy state can absorb a photon and flip to the high energy state, while electrons in the high energy state can release a photon and flip to the low energy state via stimulated emission. In a perfectly balanced system (infinite spin temperature) where there are an equal number of electrons in the spin up and spin down states, these two processes would occur at the same rate and would therefore cancel each other out, providing no net response. It is therefore clear to see how the magnitude of the EPR response is related to the spin polarization, that is, the difference in the number of electrons in the spin up and spin down states.

The ratio of the number of spins in the up state and the down state for free and isolated electrons can be approximated by

$$\frac{N_+}{N_-} = \exp\left(\frac{-g_e\mu_B B_0}{k_B T}\right) \quad (2.1.8)$$

where $k_B = 1.3806 \times 10^{-23} J/K$ and T is the absolute temperature in Kelvin. X-band EPR measurements are typically made at magnetic fields of approximately 3500 Gauss and the simplest measurements are usually made at room temperature, approximately 300 K. Since the term in the exponent is much less than one, equation 2.1.8 can therefore be simplified to be approximately

$$\frac{N_+}{N_-} = 1 - \frac{g_e\mu_B B_0}{k_B T} \quad (2.1.9)$$

using a series expansion. Using the parameters described above with the magnetic field of 3500 Gauss and an absolute temperature of 300K, this ratio is approximately $\frac{N_+}{N_-} = 0.9984$ if the g for the defect is question is close to the free electron g value. This indicates that the spin populations are very similar at room temperature; however, this level of polarization is still high

enough to detect approximately 10^{10} total paramagnetic sites. It is clear in equation 2.1.9 that increased spin polarization can be achieved by increasing the strength of the applied magnetic field and reducing the temperature of the sample.

Chapter 2.1.2 Spin Relaxation

As the spins flip due to exposure to the electromagnetic radiation satisfying the resonance condition, they are also interacting with their local environment. Electrons spins can return to their original spin populations by interacting with their surroundings in material through a process called spin relaxation. The first method is spin lattice relaxation. The time it takes for a spin system out of equilibrium to relax back to its equilibrium magnetization is described by the spin-lattice relaxation time, T_1 . Increased coupling of the electron to the lattice results in decreased T_1 times. There is a second relaxation process involving interactions between electron spins. Electron spins can interact with each other causing them to precess at slightly different rates, becoming de-phased over a spin-spin relaxation time, T_2 .

When the electrons are not allowed to relax back to a polarized state, the EPR response will vanish, therefore it is important to ensure that the correct microwave power level is used in the measurements. Electron spin populations with long T_1 times will not be able to return to a polarized state if too much microwave power is applied to them, and the signal amplitude will shrink with increasing microwave power after the spin system has been saturated. Below this saturation point, at lower microwave powers, the size of the signal will increase roughly linearly with square root of applied power, and the EPR response is said to be in the linear region.

Chapter 2.1.3 Spin Orbit Coupling and Electron Nuclear Hyperfine Interactions

Chapter 2.1.3.1 Spin Orbit Coupling

As mentioned previously, electrons in real materials do not behave like the idealized simplest case of a free electron isolated from its environment. If we consider an unpaired electron bound to an atomic nucleus, the electron will have contributions to its magnetic moment from its intrinsic quantum spin and from the motion of the electron around the nucleus. The electron's magnetic moment is described by

$$\boldsymbol{\mu}_e = g\mu_B\mathbf{S} + \mu_B\mathbf{L} \quad (2.1.10)$$

where $\mathbf{L}$ is the orbital angular momentum of the electron. The electron 'orbiting' the nucleus acts as a small current loop which in turn generates its own magnetic field around the loop. From the perspective of an observer on the electron, the nucleus appears to be travelling around it, providing an effective magnetic field which alters the magnetic moment of the electron.

This interaction between the orbital angular momentum of the electron spin and the nearby nucleus is referred to as 'spin-orbit coupling'. The amount of spin-orbit coupling experienced by an electron is measured as a change in the g factor. The deviation from the free electron g_e is more prominent in samples with larger nuclei containing more nuclear charge as well as electron spins with higher orbital angular momentum. The g factor is best described as a second rank tensor and structural information can also be gained by measuring g for different orientations in space. The g tensor is usually anisotropic in solid state materials and takes the form

$$\mathbf{g} = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix}. \quad (2.1.11)$$

In the principal axis system of the $\mathbf{g}$ tensor it takes the form of

$$\mathbf{g} = \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}. \quad (2.1.12)$$

It is these values of g_{xx} , g_{yy} , and g_{zz} in which the symmetry of a defect can be determined; as defects with axial symmetry will have two of these values be the same.

Chapter 2.1.3.2 Electron Nuclear Hyperfine Interactions

Atomic nuclei can also possess spin angular momentum, though not all do. The spin angular momentum, $\mathbf{I}$, will alter the resonance condition of an electron in a paramagnetic site. Unlike electrons, which all have spin $\frac{1}{2}$, the nuclear spin depends on the number of protons and neutrons in the nucleus. A nucleus with an even number of both protons and neutrons will have no nuclear spin moment, $\mathbf{I} = 0$. A nucleus with an odd number of protons, neutrons, or both will have a magnetic moment. An odd number of nucleons will result in a half integer nuclear spin ($I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$) while an even number of nucleons will result in an integer nuclear spin ($I = 0, 1, 2, 3, \dots$). The magnetic moment of the nuclear spin angular momentum is described by

$$\boldsymbol{\mu}_N = g_N \mu_N \mathbf{I} \quad (2.1.13)$$

where g_N is the nuclear g factor and μ_N is the nuclear Bohr magneton. The values of g_N are known for every stable atomic isotope.

Nearby nuclei with magnetic moments can align in certain orientations with a large externally applied magnetic field. A paramagnetic electron close to a nucleus with a nuclear magnetic moment will therefore experience a local magnetic field from a magnetic nucleus that differs from the externally applied field. The interaction between electrons and nearby magnetic nuclei is known as electron nuclear hyperfine interactions and is characterized by a splitting of

the measured EPR spectrum into two or more lines. If the applied field is large, magnetic nuclei will align with the applied magnetic field in $2I + 1$ orientations, giving rise to $2I + 1$ lines in a measured EPR spectrum.

An example of a spin $\frac{1}{2}$ nucleus is shown below in Figure 2.3. Notice that for a spin-0 nucleus, the dotted lines would represent the energy splitting and a single line would appear at the magnetic field corresponding to the g value of the defect at the vertical dotted line. The local magnetic field from a spin- $\frac{1}{2}$ nucleus results in two lines centered about the magnetic field corresponding to the g value of the defect.

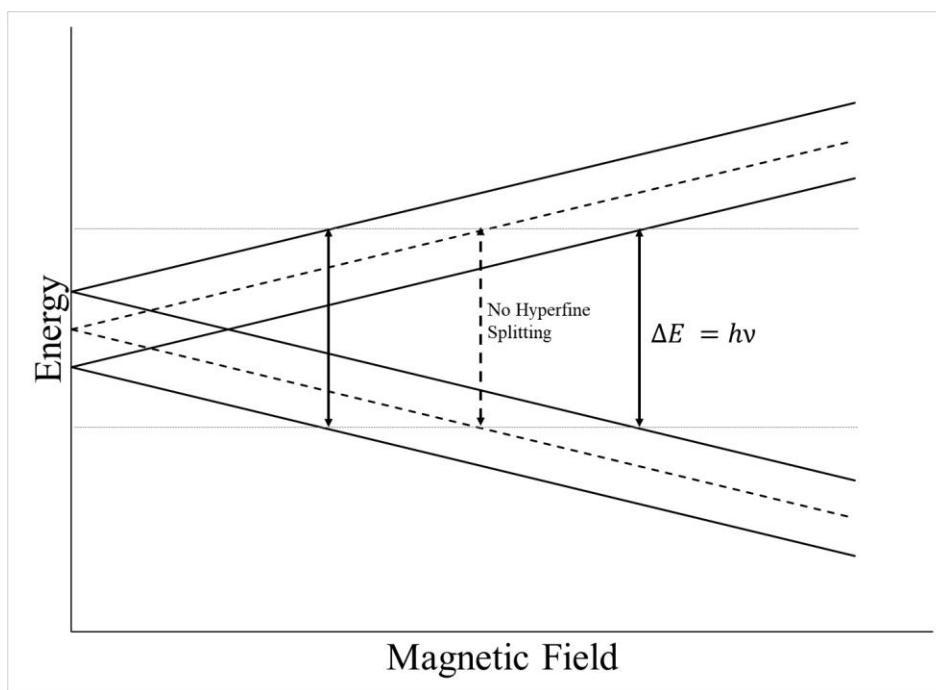


Figure 2.3: Illustration of how resonance fields are shifted by hyperfine interactions. With no hyperfine interactions (dotted line) a single line would appear at the resonance field corresponding to the g of the defect. With hyperfine interactions (solid lines) two lines appear centered about the g of the defect.

Taking these effects into account, the Hamiltonian shifts from the simple case of equation 2.1.6 to a more complex expression

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_i \mathbf{I}_i \cdot \mathbf{A}_i \cdot \mathbf{S} \quad (2.1.14)$$

where, in the second term, $\mathbf{I}_i$ is the nuclear spin operator for each nucleus, $\mathbf{A}_i$ is the hyperfine tensor for each nucleus, and $\mathbf{S}$ is, once again, the electron spin operator. Information about defect structure and chemistry can be gained by determining measured values for g and hyperfine parameters.

Chapter 2.2 Electrically Detected Magnetic Resonance

EDMR provides a method to study fully processed devices and smaller samples with magnetic resonance. EPR provides a strong analytical tool to study samples with at least 10^{10} total paramagnetic sites, however in most technologically relevant systems, there are orders of magnitude fewer defects. Alternate detection schemes can be used to get around this limitation of conventional EPR. A variant of EPR which bypasses this limitation is electrically detected magnetic resonance (EDMR). The most common EDMR experiments involve changes in spin dependent currents due to recombination or tunneling. This detection scheme has the advantage of having a higher sensitivity, usually around 10^3 total defects. The measurement can also be made on fully processed devices and is only sensitive to electrically active defects which affect electrical conduction in these devices and materials.

EDMR measurements made at X-band use most of the same equipment as the EPR measurements discussed before, with a few small additions. The detection scheme for EDMR relies on changes in the electrical characteristics of a sample as it undergoes magnetic resonance, therefore an electrical connection must be made to the sample in the microwave cavity and a current to voltage converter is used with a biasing circuit. A sample can be mounted and wire

bonded onto a specialized device holder with electrical leads allowing for the application of electrical bias and measuring sample current. Measured EDMR spectra are generated by plotting the change in the electrical current through the sample as a function of the slowly varied magnetic field, B_0 . Just like the EPR measurements discussed before, magnetic field modulation and lock-in detection are used to improve the signal to noise ratio. EDMR also has the advantage of having a sensitivity which is essentially magnetic field independent. The signal amplitude does not vary much over a wide range of resonant fields and frequencies, unlike EPR in which the signal amplitude is highly magnetic field dependent, as discussed previously. [35], [36] The two primary spin dependent currents measured are spin-dependent recombination (SDR) and spin-dependent trap assisted tunneling (SDTAT)

Chapter 2.2.1 Spin Dependent Recombination

Spin dependent recombination can be explained at a rudimentary level in terms of a slightly modified Shockley-Read-Hall model for recombination [34], [35], [45]–[47]. Electrons and holes can be captured by deep level defects within the bandgap, as seen in Figure 2.4. When an electron in the conduction band and the electron in the paramagnetic defect are polarized in the same direction, the conduction band electron cannot be captured due to the Pauli-Exclusion principle. The electron in the trap can be flipped during magnetic resonance, converting what was a triplet state into a singlet state, making the previously forbidden transition possible. The conduction electron can now be captured by the deep level defect and recombine with a hole from the valence band. An increased number of recombination events during magnetic resonance causes a measurable change in the steady state current.

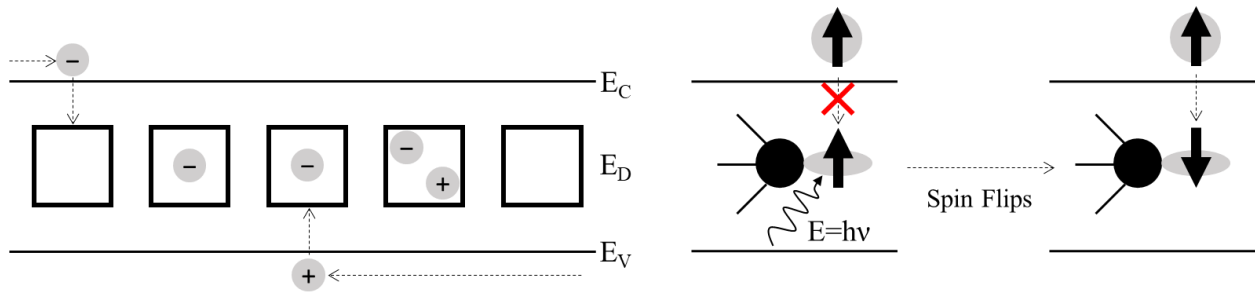


Figure 2.4: (Left) Schematic of recombination event mediated by a deep level defect. The initial electron capture is only possible if the spins of the electrons do not violate the Pauli-Exclusion principle. (Right) flipping the spin of the neutral defect can turn a forbidden transition into an allowed one.

This SDR mechanism is responsible for the signal in experiments such as the spin dependent gated diode measurements [46], [48], [49] and spin dependent charge pumping (SDCP) [50], [51]. In these experiments, the resonance signal arises from measuring the changes in the steady state currents from the electrical measurements detailed above due to magnetic resonance.

Chapter 2.2.2 Spin Dependent Trap Assisted Tunneling

Spin dependent trap assisted tunneling (SDTAT) is an EDMR measurement that relies on the spin dependent nature of VRH currents [33], [44], [49], [52]. Figure 2.5 shows that electrons cannot tunnel to a site that has an electron with the same spin orientation due to the Pauli-Exclusion principle, not unlike an electron being captured by a deep level in SDR. The electron can be flipped during magnetic resonance, allowing it to tunnel into the next site. This change in tunneling current through the material is measured during SDTAT and gives rise to the EDMR spectra associated with the defects involved.

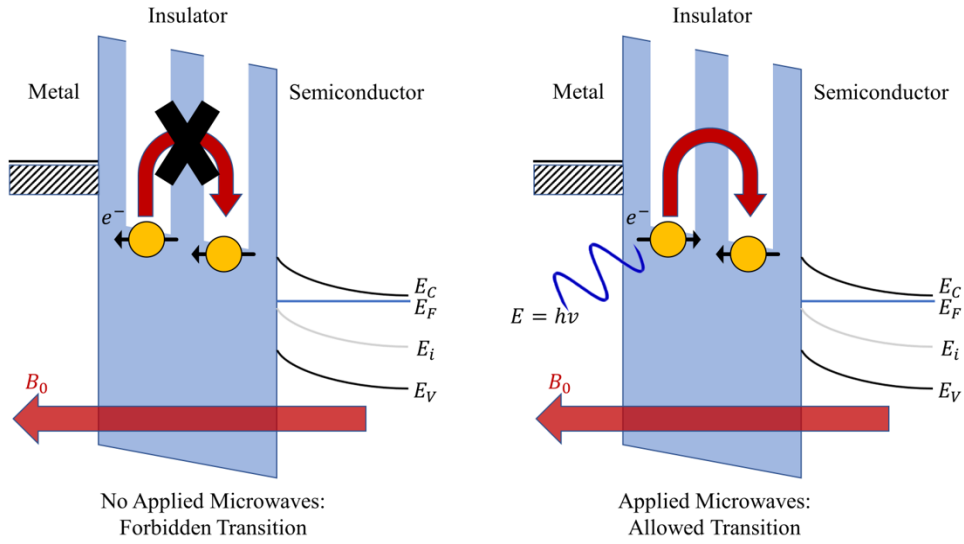


Figure 2.5: Cartoon illustration of (left) tunneling event forbidden due to Pauli-Exclusion principle and (right) allowed transition after spin flip due to magnetic resonance. Adapted from Myers et al.[53]

These different types of EDMR measurements allow for an approximate measurement of the physical region and energy levels probed during resonance measurements, as only defects that contribute to the device current will be detected while defects in the bulk and other regions that do not affect device performance will be neglected; these unimportant defects would be detected in a conventional EPR measurement assuming the quantity is high enough. The size and shape of the resonance signals (determined usually by spin orbit coupling and hyperfine interactions) provide information about physical and chemical nature of the defects in the device. EDMR has been utilized extensively to study defects in semiconductor devices [33], [37], [41], [44], [46], [48], [51]–[56].

Chapter 3

Near Zero Field Magnetoresistance in Inorganic Semiconductors and Dielectrics

All of the spin dependent measurements outlined above appear to give signals at near zero magnetic field as well as at resonance. Magnetoresistance is a change in the electrical conductivity of a material at low applied magnetic fields. It is not as well understood as conventional EPR and EDMR measurements; however, some models have been put forward to explain the phenomenon of organic magnetoresistance (OMAR) in positionally disordered organic semiconductors [57]–[62]. Unlike EDMR measurements, in NZFMR, the shift from a forbidden to an allowed transition is not caused by flipping spins at resonance, but by a mixing of states due to variations in local magnetic fields. The models for OMAR presented so far focus on unipolar transport through disordered organic materials, which is qualitatively very similar to SDTAT in inorganic semiconductors outlined above. These similarities make amorphous inorganic semiconductors an ideal choice to use to adapt the current OMAR models and expand our knowledge of NZFMR.

Chapter 3.1 Magnetoresistance in Organic Materials

Current proposed models for OMAR suggest that charge carriers attempt to move across a disordered material by hopping from site to site, like a network of random resistors similar to the model put forward by Miller and Abrahams [63]. In this model, the bulk conductivity is set by the distance between sites that a charge carrier must move between to get across the device. A critical distance, r_c is defined as the longest allowed hopping distance required to form a path through the material. Longer critical hopping distances lead to lower conductivity. Two localized charge carriers in adjacent sites are referred to as a polaron pair while a doubly

occupied site is referred to as a bipolaron. A polaron may only hop to another polaron's site, forming a bipolaron, if the polaron pair is in the singlet configuration because of the Pauli-Exclusion principle. In the presence of a magnetic field that aligns electron spins, certain hops can be blocked if the polaron attempts to hop to a site occupied by a polaron with the same spin orientation, or the polaron pair is in a triplet state. This is referred to by Harmon and Flatté as spin blocking [60]–[62] and is the foundation of magnetoresistance in disordered organic semiconductors.

The model proposed by Harmon and Flatté is similar to a two-site model proposed by Wagemans et al. [58] which was expanded upon by Schellekens et al. [59] in which the relative spin projection of charge carriers in adjacent sites can change due to local hyperfine fields. In the case of organic semiconductors, these hyperfine interactions primarily come from randomly oriented hydrogen nuclei. Each site has a magnetic field that is the vector sum of the local random hyperfine field and the externally applied field. At low and zero applied magnetic fields, the charge carriers will precess about their individual random hyperfine fields allowing a triplet state to gain more singlet character as the relative orientation of the spins change. A large applied magnetic field will suppress the random hyperfine fields and the polarons on different sites will experience almost identical local magnetic fields. When the local field is overwhelmed by the applied field, the polaron spins will precess about near identical magnetic fields, suppressing any spin mixing. In this case polaron pairs in the triplet state will remain that way and be unable form bipolarons, as illustrated in Figure 3.1.

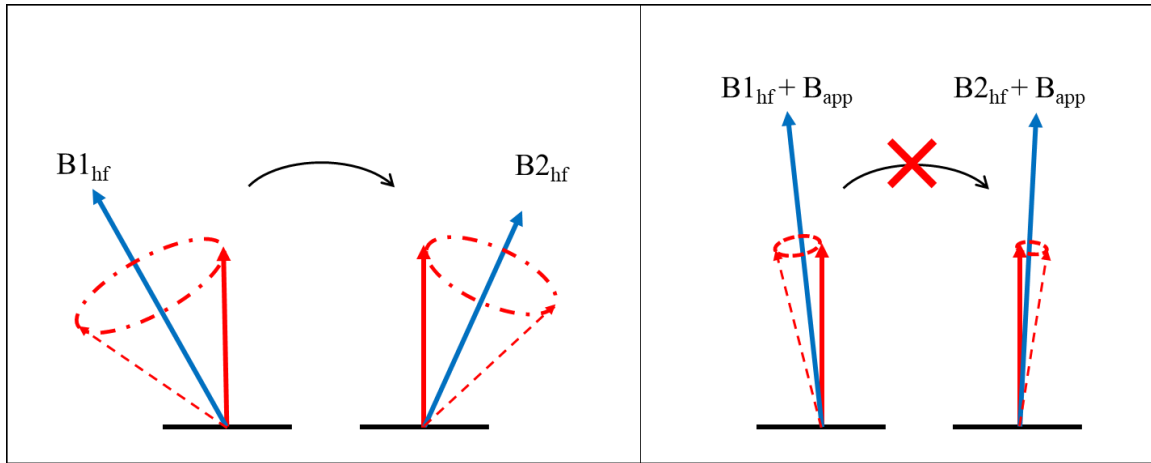


Figure 3.1: Spin mixing due to hyperfine fields. Left) Spins precess coherently about random hyperfine fields alternating between all triplet character (solid red line) and partial singlet character (dotted red line) allowing for hopping to occur. Right) Spins precess about similar magnetic fields maintaining more of their triplet character, preventing hopping. Recreated from Schellekens et al. [59]

Current through the material will increase as more hopping sites are accessible and it will decrease when there are fewer, therefore as previously forbidden hopping sites become available due to triplet to singlet transitions at low applied magnetic fields, the current will be larger than at high applied magnetic fields where such transitions do not occur and hopping distances through the material will be longer. This concept is illustrated in Figure 3.2. Formation of bipolarons leads to increased conduction.

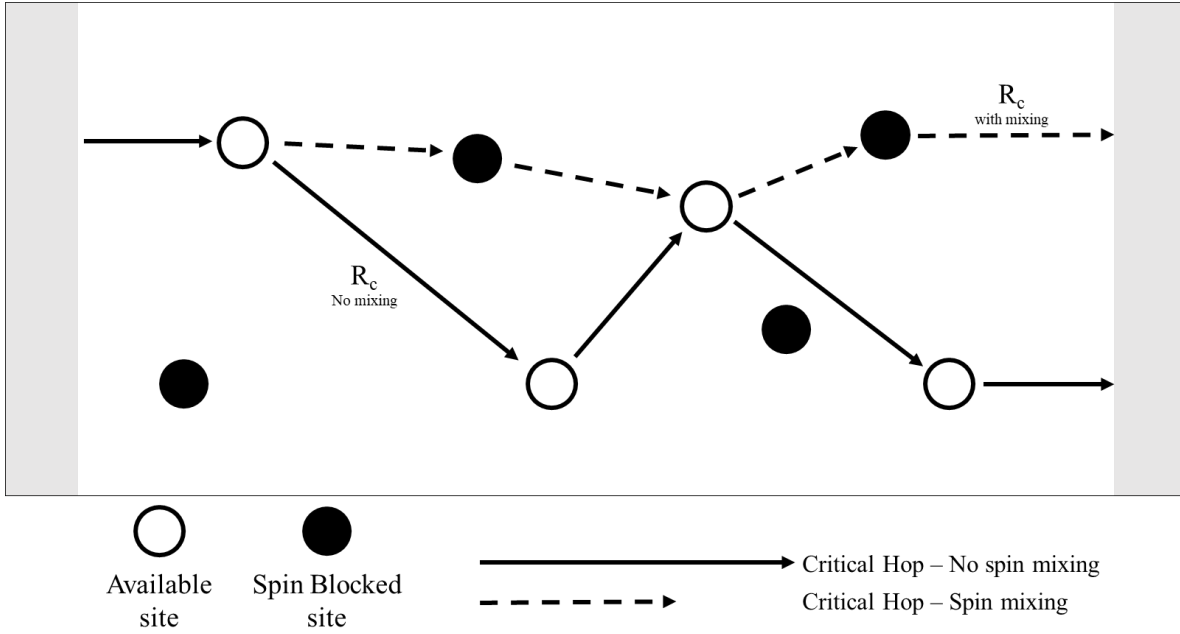


Figure 3.2: Illustration of spin blocking. The solid line represents the hopping path without spin mixing as spin blocked sites are inaccessible. The dotted line represents a possible hopping path with spin mixing as the spin blocked sites can transition to available sites as the spins precess in local hyperfine fields. The longer critical hopping distance due to blocked sites causes an increase in the resistance of the material. Recreated from Harmon and Flatté. [61]

Magnetoresistance is quantified by utilizing the density matrix formalism. The density operator for a simple two site model with an ensemble of N spins can be written as:

$$\rho = \frac{1}{N} \sum_{n=1}^N |\psi_n\rangle\langle\psi_n| \quad (3.1.1)$$

Choosing an orthonormal basis set φ_i allows us to define the density matrix as:

$$\rho_{i,j} = \langle \varphi_i | \rho | \varphi_j \rangle \quad (3.1.2)$$

The probability of finding the system in the corresponding basis states is given by the diagonal elements of the density matrix. The system will evolve coherently over time as the spins precess according to the time dependent Schrodinger equation and is described by the quantum Liouville equation:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] \quad (3.1.3)$$

where H is the spin pair Hamiltonian [59], and $[H, \rho]$ is commutator of the Hamiltonian and the density matrix.

For a system in which spin pairs are formed and removed over time, it is necessary to include these phenomena in the equation governing the time evolution of the system which is achieved by utilizing the stochastic Liouville equation (SLE):

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{2} \{\Lambda, \rho\} + \Gamma \quad (3.1.4)$$

where $\{\Lambda, \rho\}$ is the anticommutator of the projection operator, Λ , and ρ , the first term is the coherent time evolution with no other interactions as seen in (3.1.3), the second is a dissipative term that removes spin pairs from the system, and the last is a generation term. OMAR is a steady state process and magnetoresistance values are determined by tracking the population of spins in the density matrix, ρ , for long time scales. In these unipolar models, increased bipolaron formation at low applied magnetic fields leads to increased hopping and therefore increased current.

Chapter 3.2 NZFMR Models in Solid State Materials

The models described above have been somewhat expanded in some material systems by Frantz et al. [64] and Harmon et al. [65]. The stochastic Liouville equation utilized in these models is the same as the previously described models.

Chapter 3.2.1 Electron-Hole Spin Dependent Recombination Model for NZFMR

This model [64] is based on a combination of the models put forward by Prigodin et al. [66] and Harmon and Flatté [62]. This model describes spin dependent recombination which occurs at deep level defects in inorganic materials. The model is similar to that shown in Figure 2.4 which illustrates spin dependent recombination due to resonance. An electron in the conduction band can approach a deep level defect with an unoccupied electron orbital near a nucleus with a nuclear spin and associated hyperfine field. This nuclear spin is represented by the blue arrows in Figure 3.3. The free electron can be temporarily captured in an intermediate state just below the conduction band where it can then attempt to enter the deep level defect. If the free electron and the defect electron are in the same spin orientation, a triplet state, the free electron will be unable to be captured by the trap. However, if the two electrons have opposite spin orientations, a singlet state, the free electron can then be captured by the deep level. Unlike in EMDR, the transition from a triplet state to a singlet state does not come from impinging electromagnetic radiation, but from spin mixing of the defect electron due to local magnetic fields, as described in Figure 3.1. If a singlet is formed due to spin mixing, the free electron will drop into the deep level and then recombine with a hole in the valence band, removing the electron and hole from the system. This essentially causes the spins to be annihilated. If the spin pair does not form a singlet and remains in the triplet state, then the free electron can dissociate from the intermediate state and return to the conduction band, causing no change to the recombination current. Increased spin mixing at low applied magnetic fields will cause the recombination current to increase as more spin pairs transition from triplet to singlet states. This process is illustrated in Figure 3.3.

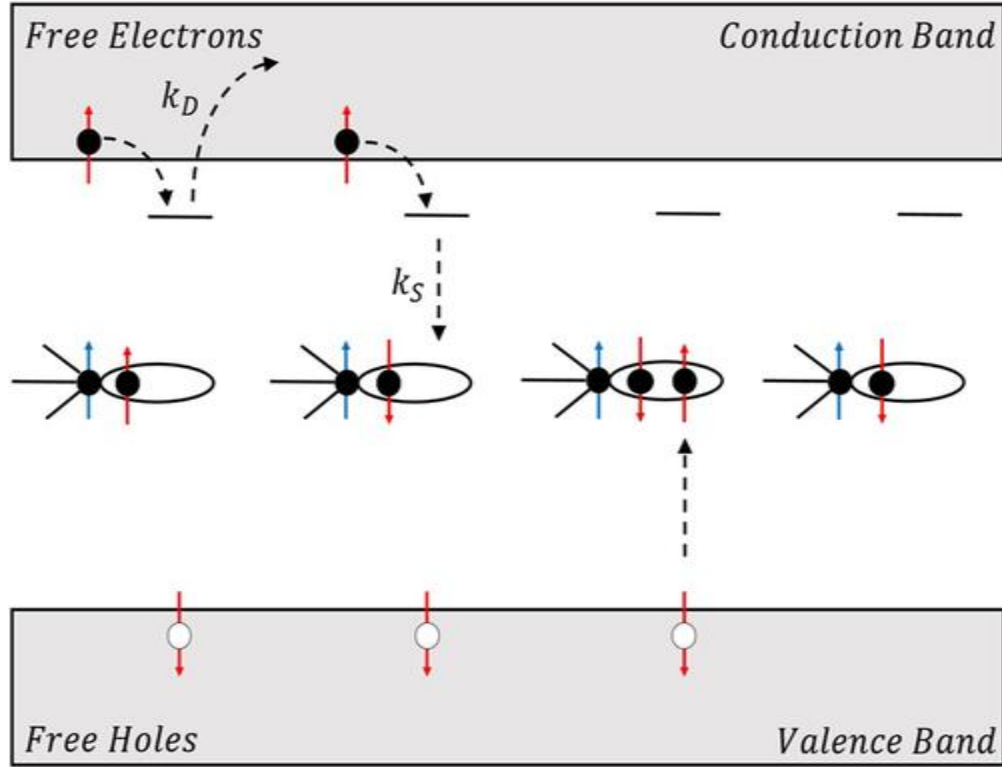


Figure 3.3: Model for near zero field magnetoresistance spin dependent recombination. Note the nuclear magnetic moment indicated by the blue arrows on the atomic nuclei. Adapted from Frantz et al. [64].

The density matrix in this model evolves in a manner described by an adapted form of the SLE first discussed by Hansen and Pendersen [67]

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathbf{H}, \rho] - \frac{1}{2} (k_S + k_D) \{\mathbf{A}_S, \rho\} - \frac{k_D}{2} \{\mathbf{A}_T, \rho\} + \frac{1}{8} p \Gamma \quad (3.2.1)$$

where the first term represents the coherent evolution of the spin pairs due to local magnetic fields, the second term is a dissipative term that removes singlet electron hole pairs from the system at a rate of k_S through recombination, the third term is also dissipative which removes triplets in which the free electron has dissociated from the intermediate state back to the conduction band at a rate of k_D , $\mathbf{A}_S$ and $\mathbf{A}_T$ are the singlet and triplet projection operators, respectively, and the fourth term is a generation term that represents a source of carriers which

enter the system at a rate of p and $\mathbf{I}$ represents the spin populations of the generated pairs. For randomly generated spin pairs, $\mathbf{I}$ is the identity matrix. The last term has a factor of $\frac{1}{8}$ so that the total generation rate of all the spin pairs is equal to p since the identity matrix is 8×8 . This is a steady state process in which spins are being generated and removed at constant rates so only the steady state form of equation 3.2.1 needs to be solved,

$$0 = -\frac{i}{\hbar} [\mathbf{H}, \boldsymbol{\rho}] - \frac{1}{2} (k_S + k_D) \{\mathbf{A}_S, \boldsymbol{\rho}\} - \frac{k_D}{2} \{\mathbf{A}_T, \boldsymbol{\rho}\} + \frac{1}{8} p \mathbf{I}. \quad (3.2.2)$$

Assuming that only the defect electron is affected by the local nuclear hyperfine interactions, the Hamiltonian for such a spin system is

$$\mathbf{H} = g\mu_B(\mathbf{S}_1 + \mathbf{S}_2) \cdot \mathbf{B} + a(\mathbf{S}_2 \cdot \mathbf{I}) \quad (3.2.3)$$

where $g\mu_B(\mathbf{S}_1 + \mathbf{S}_2)$ accounts for the Zeeman splitting due to the applied magnetic field, $\mathbf{B}$, of both the electron in the conduction band, $\mathbf{S}_1$, and of the electron in the defect, $\mathbf{S}_2$, and $a(\mathbf{S}_2 \cdot \mathbf{I})$ represents an isotropic electron-nuclear hyperfine interaction with strength a between the defect electron and the magnetic nucleus, $\mathbf{I}$. The solution to the steady state SLE for NZFMR SDR will be explored in Chapter 3.2.3.

Chapter 3.2.2 Spin Dependent Trap Assisted Tunneling Model for NZFMR

To model the NZFMR response in samples where the primary conduction method is trap assisted tunneling, the two-site model proposed by Wagemans et al. [58] was adapted by Frantz et al. [64]. Carriers that travel through a material via trap assisted tunneling will use many sites on the path across the material, but the conduction through the material can generally be limited most by the longest hop, like the two-site model for OMAR described above. It is not unreasonable to focus on this bottleneck spin pair when modeling the SDTAT NZFMR response.

The adapted two-site model is shown in Figure 3.4. The model consists of two sites around nuclei that electrons can occupy, sites α and β . The nuclei at both α and β sites have nuclear spins represented by the blue arrow resulting in hyperfine fields experienced by the electrons on that site. The hyperfine coupling constants for each site when occupied by an electron are a_α and a_β for the sites α and β respectively. An electron from the environment can hop to site α when it is unoccupied at a rate of $r_{e\alpha}$. Once the electron is on site α it will interact with the local hyperfine interaction by precessing about it, this is shown in Figure 3.4 with the red arrow and the dashed path that it follows around the hyperfine field. The electron trapped at site α can either jump directly to the environment at a rate of $r_{\alpha e}$ or it can hop to site β at a rate of $P_S r_{\alpha\beta}$, where P_S is the probability of the electrons at sites α and β to be in the singlet configuration. If the electron hops from site α to site β , the electron that is now at site β can then jump out of that site and into the environment at a rate of $r_{\beta e}$. All of these paths and rates are shown in Figure 3.4

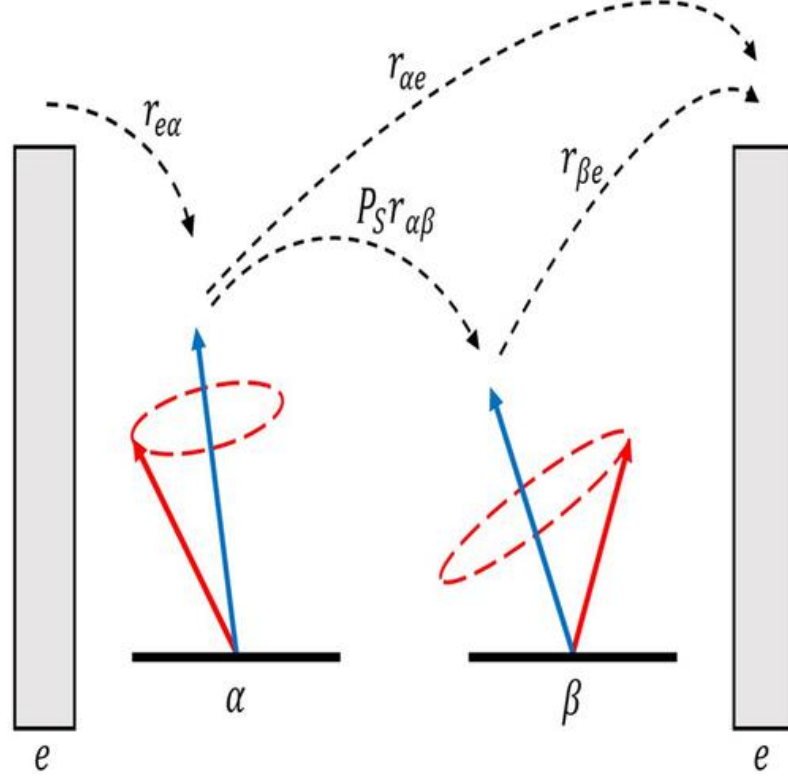


Figure 3.4: Two site model for spin mixing of electrons in NZFMR SDTAT. The blue arrows indicate the hyperfine fields from the atomic nuclei, the red arrows indicate the electron spin orientations. The red dashed lines indicate the precession of the electron spins as they evolve coherently due to the local hyperfine magnetic fields. Adapted from Frantz et al. [64]

The trap assisted tunneling current is defined as the flow of carriers from the environment on the left of Figure 3.4 to site α . There will almost always be a state available in the environment for an electron in site β to hop to, so $r_{\beta e}$ is set to ∞ in order to make the arithmetic simpler.[59]

With this simplification, the equation governing the density matrix of the spin system is the SLE adapted from [58] and has the form

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathbf{H}, \rho] - \frac{1}{2} (r_{\alpha\beta} + r_{\alpha e}) \{\mathbf{A}_S, \rho\} - \frac{1}{2} r_{\alpha e} \{\mathbf{A}_T, \rho\} + \frac{1}{16} r_{e\alpha} (1 - \text{Tr}(\rho)) \mathbf{I} \quad (3.2.4)$$

where $\mathbf{A}_S$ and $\mathbf{A}_T$ are once again the singlet and triplet projection operators respectively and $\mathbf{I}$ is once again defined as the identity matrix for generating spin states in random orientations. If the trap states remain mostly empty during the hopping process (as is the case in this proposed model), then $Tr(\rho) \ll 1$, and can be ignored. Like the model for SDR NZFMR, the processes involved in SDTAT NZFMR are at the steady state and therefore only the steady state form of the simplified equation needs to be solved,

$$0 = -\frac{i}{\hbar}[\mathbf{H}, \rho] - \frac{1}{2}(r_{\alpha\beta} + r_{\alpha e})\{\mathbf{A}_S, \rho\} - \frac{1}{2}r_{\alpha e}\{\mathbf{A}_T, \rho\} + \frac{1}{16}r_{e\alpha}\mathbf{I}. \quad (3.2.5)$$

Unlike the SDR model, the SDTAT model accounts for two nuclear spins, raising the total number of spins in the system to four, even if one of the nuclei has a spin of 0. The four spins interacting with each other means that the identity matrix $\mathbf{I}$ must be a 16x16 matrix and a factor of $\frac{1}{16}$ must be included to account for it. The Hamiltonian for this spin system is described by

$$\mathbf{H} = g\mu_B(\mathbf{S}_1 + \mathbf{S}_2) \cdot \mathbf{B} + a_\alpha(\mathbf{S}_1 \cdot \mathbf{I}_\alpha) + a_\beta(\mathbf{S}_2 \cdot \mathbf{I}_\beta) \quad (3.2.6)$$

where the first term is once again the Zeeman splitting of electrons at sites α and β , the second term is the isotropic electron-nuclear hyperfine interaction between the electron and nuclear spin at site α , and the third term is the electron-nuclear hyperfine interaction between the electron and nuclear spin at site β .

Chapter 3.2.3 Solution of SLE in NZFMR Models

The models put forward by Frantz et al. [64] are governed by SLEs that can be algebraically manipulated into the form of the time-continuous Lyapunov equation

$$\mathcal{L}\rho + \rho\mathcal{L}^\dagger = g \quad (3.2.7)$$

where $\mathcal{L}^\dagger$ is the conjugate transpose of $\mathcal{L}$ which is given by

$$\mathcal{L} = \frac{i}{\hbar} \mathbf{H} + \frac{c_1 + c_2}{2} \mathbf{A}_S + \frac{c_2}{2} \mathbf{A}_T \quad (3.2.8)$$

and c_1 and c_2 represent the rate constants that depend on the form of the SLE being solved, either for SDR or SDTAT. The right side of equation 3.2.7, g , represents the rate that spins are generated. This equation has a known analytic solution of

$$\rho = \int_0^\infty e^{-i\mathcal{L}\tau} (g\mathbf{I}) e^{i\mathcal{L}^\dagger\tau} d\tau. \quad (3.2.9)$$

For the SDR NZFMR, the observable change in current occurs when singlets are formed and recombination occurs, therefore the change in current will be proportional to the product of the singlet formation probability and the trace of the singlet population of the density-matrix given by

$$I_{SDR} \propto \left(\frac{k_S}{p}\right) Tr(\mathbf{A}_S \rho) \quad (3.2.10)$$

where a scaling constant can be utilized when modeling a spectrum that arises from multiple conduction paths. The measurable change in SDTAT current will be proportional to the product of the rate at which sites are filled and the probability of the occupation of the sites, therefore the change in current will be given by

$$I_{SDTAT} \propto r_{e\alpha} (1 - Tr(\rho)). \quad (3.2.11)$$

These models utilize a least squares fitting to determine what the most likely interactions are between the spins in the system to produce the measured spectrum. The majority of the samples studied in this work were thin films subjected to SDTAT NZFMR and SDTAT EDMR measurements at X-band and low-magnetic-field.

Chapter 3.2.4 SDTAT NZFMR Simulations

The model for SDTAT NZFMR put forward by Frantz et al. [64] was utilized to simulate NZFMR spectra across a range of values for the variables $r_{e\alpha}$, $r_{\alpha e}$, $r_{\alpha\beta}$, a_α , and a_β in equations 3.2.5 and 3.2.6. The values used in these simulations are $r_{e\alpha} = 1 \text{ GHz}$, $r_{\alpha e} = 0.1 \text{ GHz}$, $r_{\alpha\beta} = 1 \text{ GHz}$, $a_\alpha = 1 \text{ mT}$ (10 Gauss), and $a_\beta = 1 \text{ mT}$ (10 Gauss) unless otherwise stated. The measurements made in the later chapters will be compared to these simulated spectra to identify how changing experimental parameters affect the variables from equations 3.2.5 and 3.2.6; for example, if the changes in a measured spectra as a function of bias or time match the trends seen in these simulations, we may be able to understand the physical processes that occur to cause the change in the experimentally measured spectra.

Chapter 3.2.4.1 Simulated effects of $r_{e\alpha}$

The generation rate at which carriers are injected from the environment, or a large pool of randomly oriented carriers, into the first hopping site is given by $r_{e\alpha}$ in Figure 3.4. This can essentially be thought of as how fast carriers arrive to the sites that form the rate limiting step in the hopping transport. A large value of $r_{e\alpha}$ indicates that there are a lot of charge carriers entering the first site in the adapted two site model. Smaller values of $r_{e\alpha}$ indicate that there are less carriers entering the first site. The value of $r_{e\alpha}$ will likely also affect the overall DC current through a sample, with higher values corresponding to higher currents. The effect of varying $r_{e\alpha}$ over a range of values is shown in Figure 3.5. The fixed value for $r_{\alpha\beta}$ was changed to 0.3 GHz for this plot.

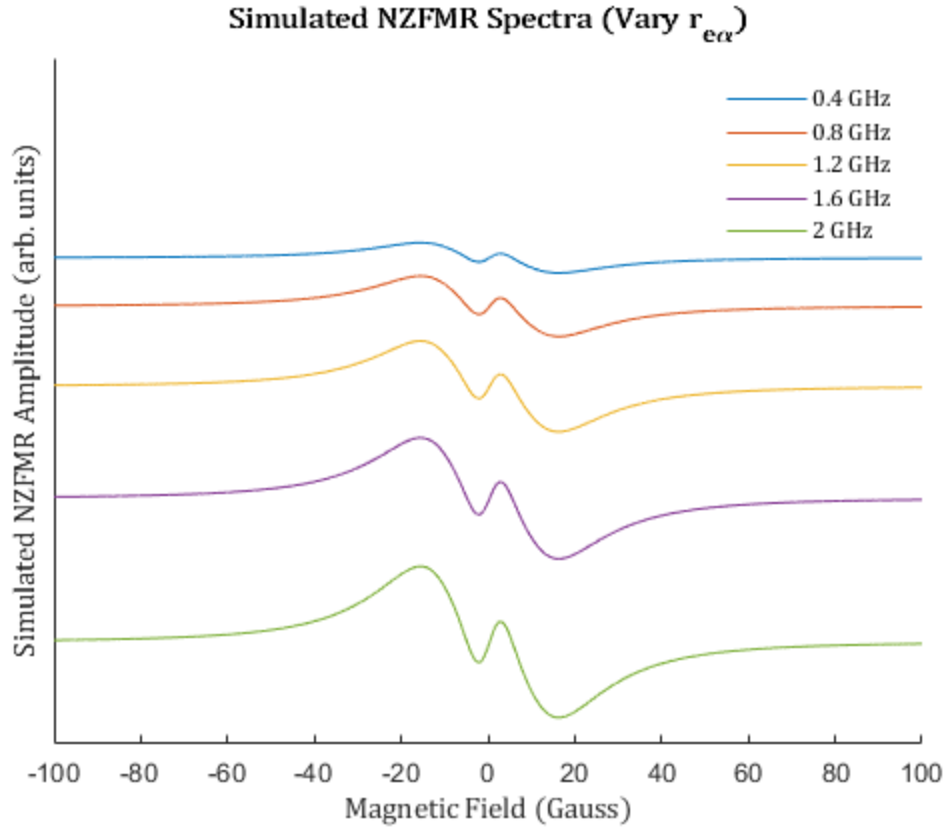


Figure 3.5: Raw simulated NZFMR spectra for different values of $r_{e\alpha}$. The order shown in the legend matches the order of the plots.

It is clear to see that increasing $r_{e\alpha}$ has the effect of increasing the NZFMR signal amplitude. The effect that $r_{e\alpha}$ has on the shape and width of the NZFMR signal can be seen more easily by normalizing these spectra. The normalized spectra are shown in Figure 3.6. In this case, the normalized spectra would overlap perfectly if not for the artificial offset. These two figures suggest that an NZFMR signal that changes only in amplitude, and not in shape, is most likely affected by a change in the rate, $r_{e\alpha}$, which primarily controls the signal amplitude of the spectrum.

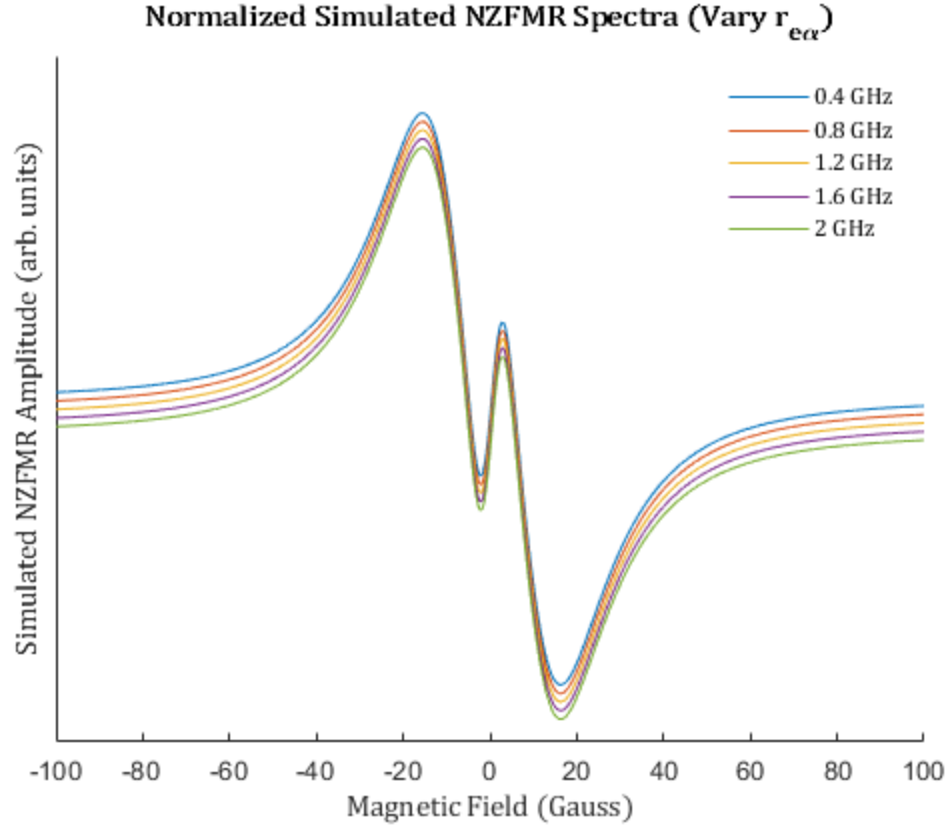


Figure 3.6: Normalized simulated NZFMR spectra for different values of $r_{e\alpha}$. The order shown in the legend matches the order of the plots. All spectra overlap perfectly without the added offset.

Chapter 3.2.4.2 Simulated effects of r_{ae}

Once a charge carrier reaches the rate limiting step in the hopping transport at site α , it can either dissociate by going directly to the environment at a rate of r_{ae} or it can hop to the next defect site, site β , at a rate of $P_S r_{\alpha\beta}$. The latter case will be discussed in detail in the next section. The rate r_{ae} can be thought of as the rate at which a charge carrier at site α is able to bypass the jump to site β and jump to larger pool of carriers. For the two-site model, this process is not spin dependent. The effects of changing r_{ae} are shown in Figure 3.7. The primary effect of increasing r_{ae} is a decrease in the amplitude of the center inflection line while the broader line remains almost constant.

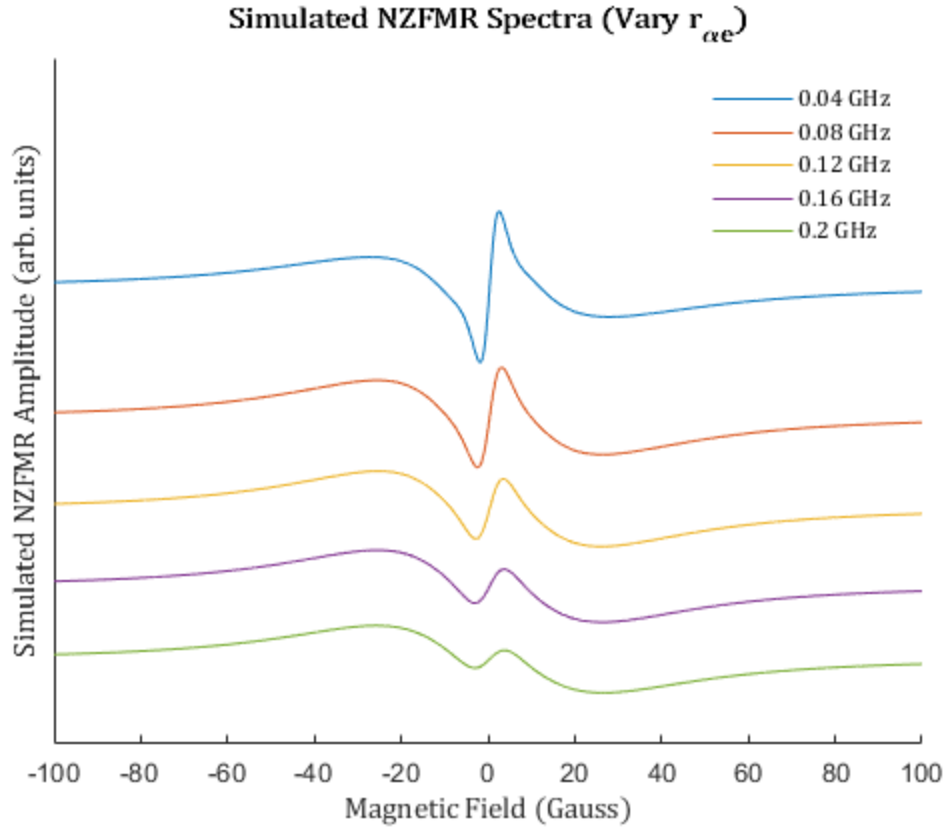


Figure 3.7: Raw simulated NZFMR spectra for different values of $r_{\alpha e}$. The order shown in the legend matches the order of the plots.

The effect of $r_{\alpha e}$ on the line shape is more easily seen when these spectra are normalized and superimposed on one another. Unlike the case of changing $r_{e\alpha}$, the normalized spectra do not overlap and so the simulated spectra were normalized twice. First, they were normalized to the broader signal in order to see how the width and shape of the broad signal change with $r_{\alpha e}$. This is shown in the top of Figure 3.8. There is very little change in the shape of the broader line due to changes in $r_{\alpha e}$. The spectra were then normalized to the narrow inflection signal in order to see how the width and shape of that signal change with $r_{\alpha e}$. This is shown in the bottom of Figure 3.8. Once again, the line width of the inflection line is almost constant as $r_{\alpha e}$ changes.

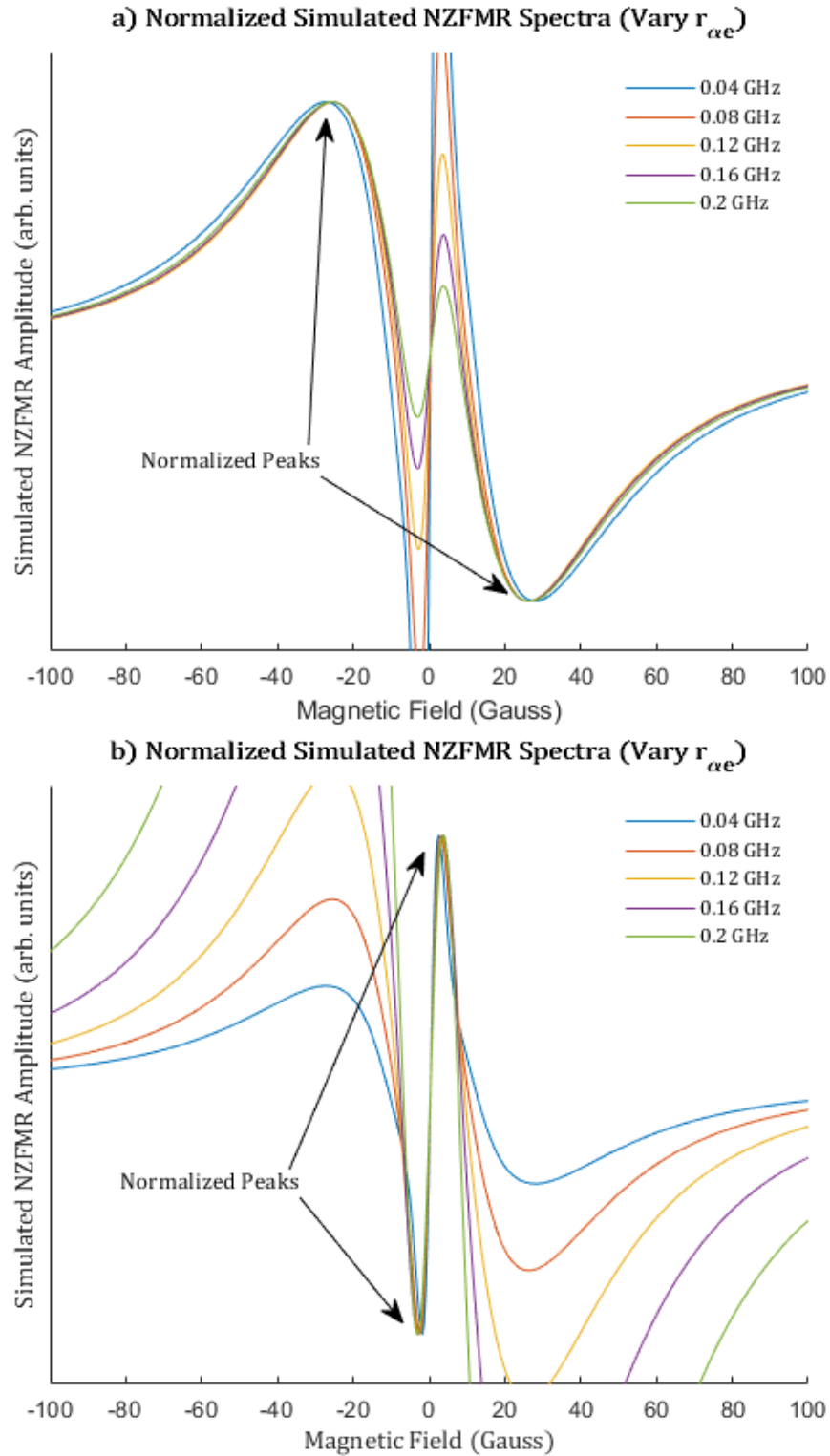


Figure 3.8: Normalized simulated spectra for different values of r_{ae} . a) Spectra normalized to the broader line to show changes in broad line shape. b) Spectra normalized to inflection line to show changes in inflection line shape. The shapes of both lines change little for different values of r_{ae} .

Chapter 3.2.4.3 Simulated Effects of $r_{\alpha\beta}$

The rate $P_S r_{\alpha\beta}$, is the singlet probability hopping rate, for which charge carriers hop from the initial site, site α , to the next site, site β . P_S is the singlet projection operator of one onto the other, as unlike the transport associated with $r_{\alpha e}$, the hops associated with $r_{\alpha\beta}$ are spin-dependent. P_S will change over time as the system evolves coherently and incoherently. The more singlet character between the charge carriers on site α and β , the higher the chance that the hopping event will occur due to the Pauli Exclusion principle. The effects of $r_{\alpha\beta}$ on the simulated spectra is shown in Figure 3.9. The overall amplitude of both the broad line and the inflection line decrease as $r_{\alpha\beta}$ is increased, however, the amplitude of the inflection line appears to decrease more slowly. These spectra were then normalized in order to see the effects of $r_{\alpha\beta}$ on the shape of the spectra. The plots in Figure 3.10 show the spectra normalized to the broad line (top) and the inflection line (bottom). It is clear to see that the broad line becomes wider for larger values of $r_{\alpha\beta}$, while the width of the narrow inflection line is essentially unchanged.

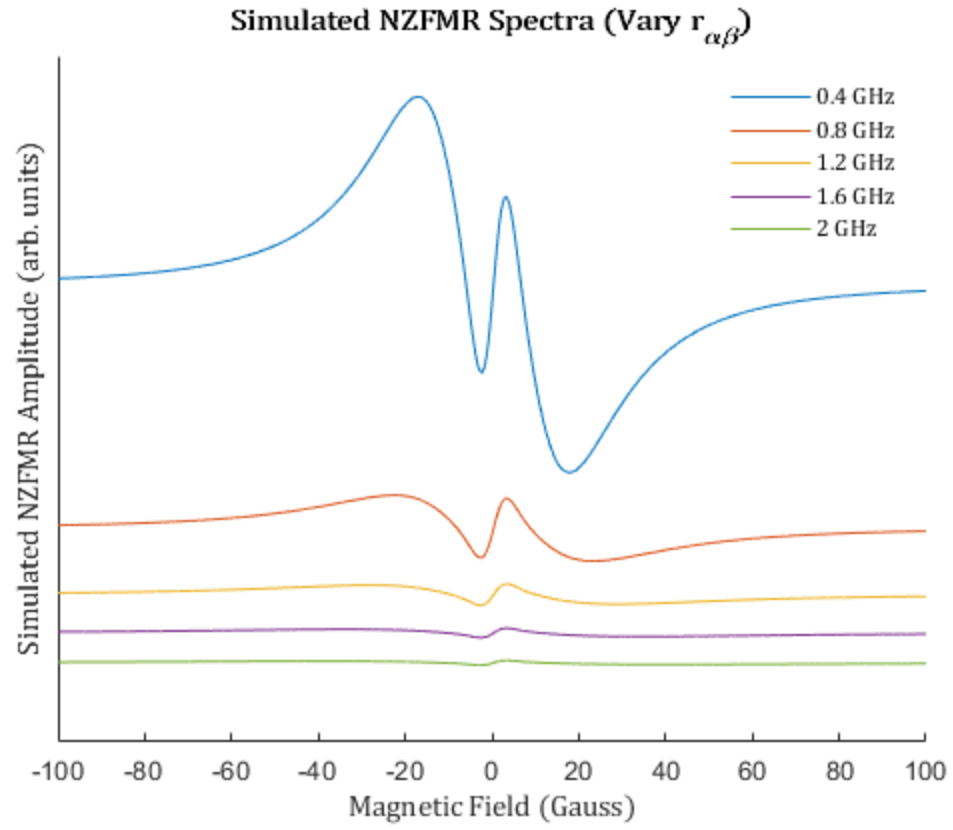


Figure 3.9: Raw simulated NZFMR spectra for different values of $r_{\alpha\beta}$. The order shown in the legend matches the order of the plots.

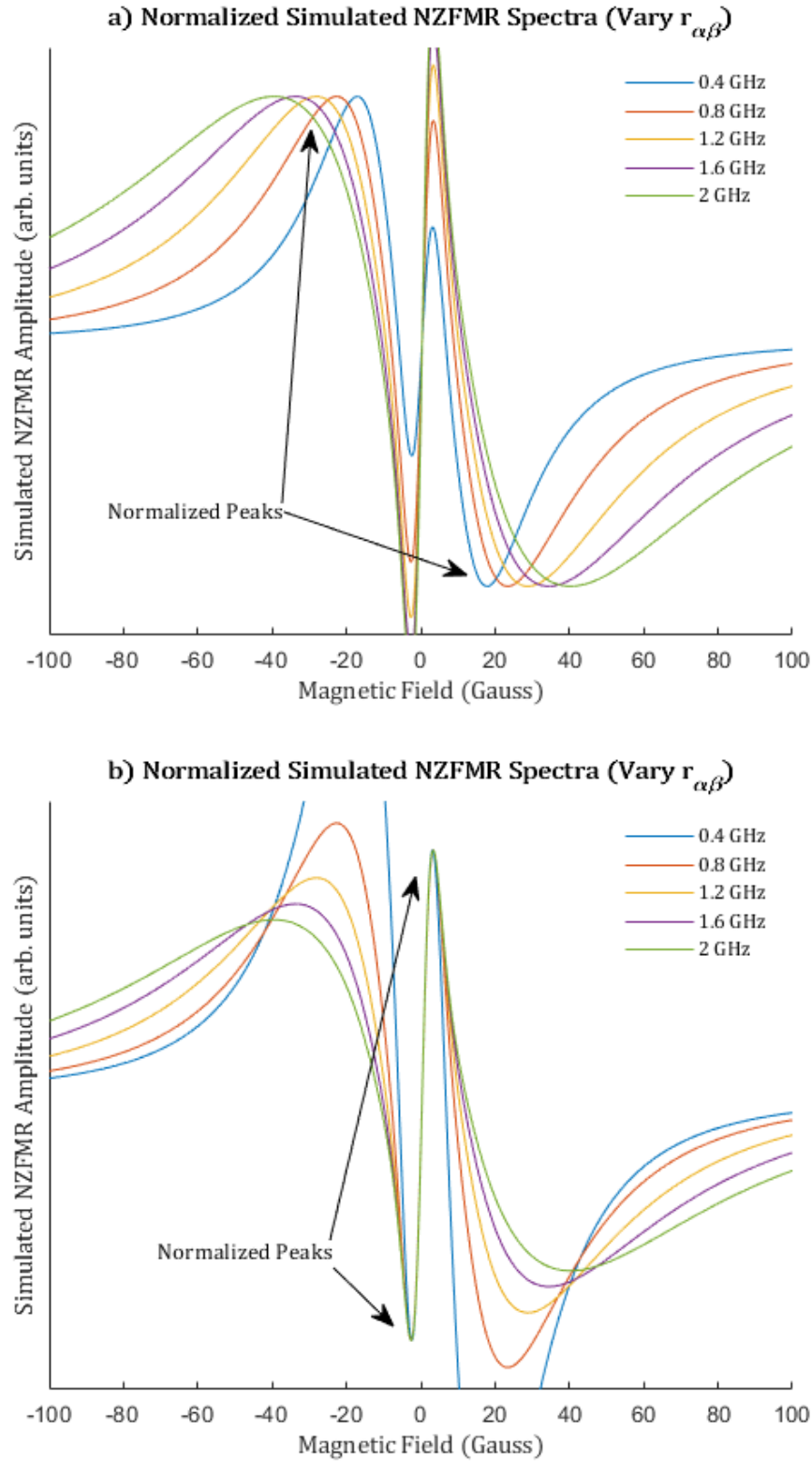


Figure 3.10: Normalized simulated spectra for different values of $r_{\alpha\beta}$. a) Spectra normalized to the broader line to show changes in broad line shape. b) Spectra normalized to inflection line to show changes in inflection line shape. The broad line width increases however the inflection line width is unchanged for increasing values of $r_{\alpha\beta}$.

Chapter 3.2.4.4 Simulated Effects of One Magnetic Nucleus

The hyperfine coupling constant between the magnetic nuclei at site α and a charge carrier at the same site is given as a_α . Large values of a_α indicates that a large magnetic field is experienced by the charge carrier due to the nearby magnetic nuclei is. This section discusses the effect of a single magnetic nucleus at site α and a non-magnetic nucleus at site β . The effect of the hyperfine coupling at site α on the simulated spectra is shown in Figure 3.11. Larger hyperfine interactions lead to more spin mixing and therefore larger signal amplitudes. The amplitude of the inflection line appears to become larger relative to the amplitude of the broad line as well. These spectra were then normalized to the broad line and the inflection line to see how the hyperfine interactions affect the shape and width of the lines. The spectra normalized to the broad line are shown in the top of Figure 3.12 and the spectra normalized to the inflection line are shown in the bottom of Figure 3.12. It is clear to see that larger hyperfine interactions cause both the broad lines and inflection lines to become wider. Hyperfine interactions are unlikely to change over the course of a study unless new defects with different interactions are introduced during the study.

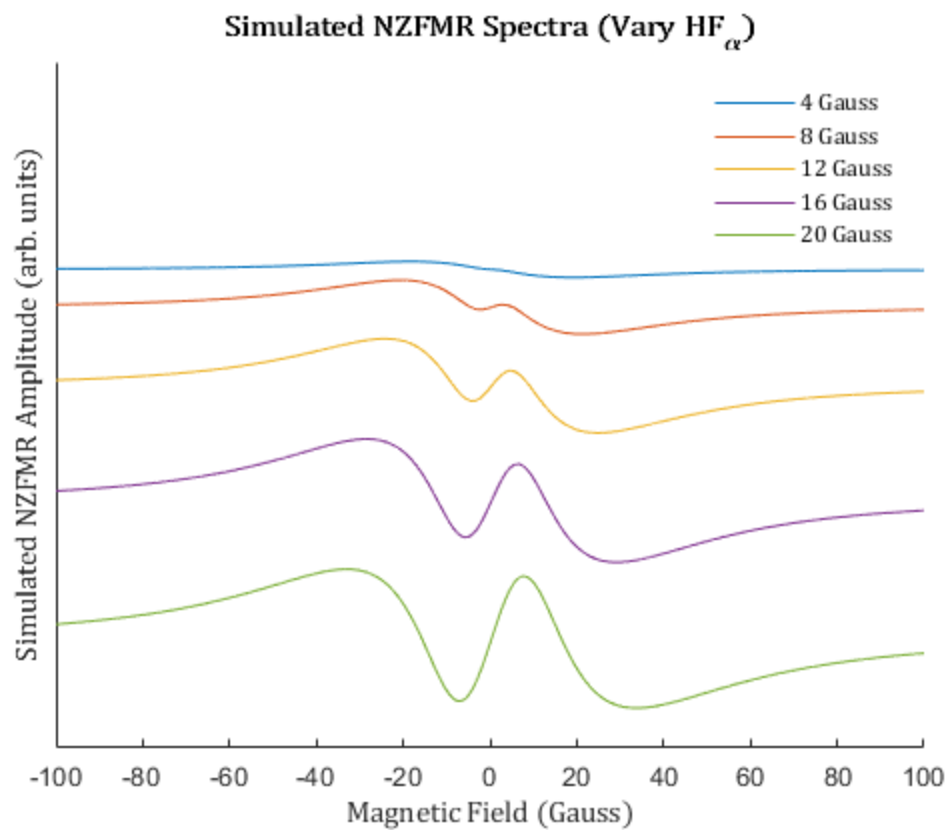


Figure 3.11: Raw simulated NZFMR spectra for different hyperfine values at site α with a non-magnetic nucleus at site β . The order shown in the legend matches the order of the plots.

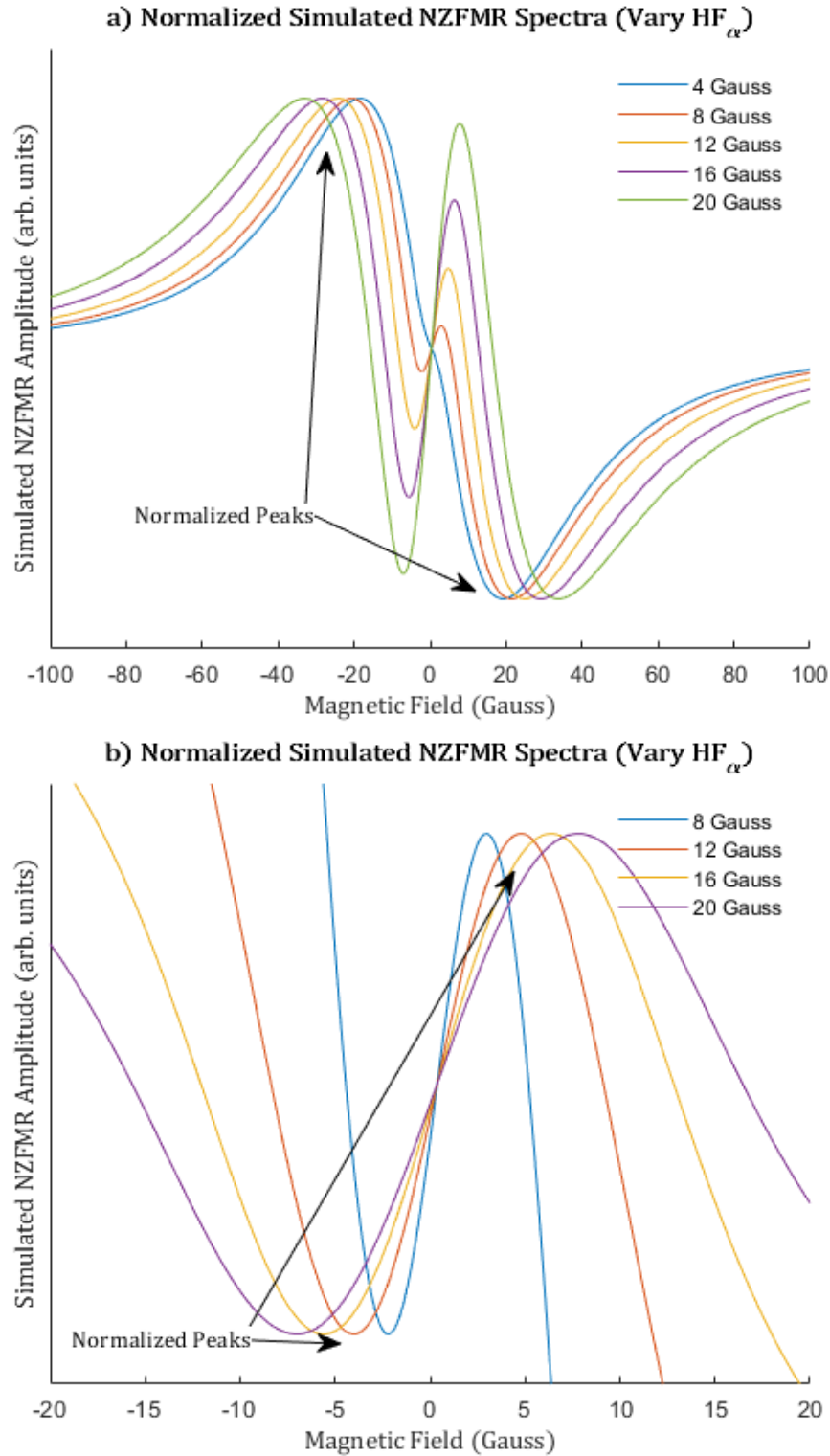


Figure 3.12: Normalized simulated spectra for different hyperfine values at site α with a non-magnetic nucleus at site β a) Spectra normalized to the broader line to show changes in broad line shape. b) Spectra normalized to inflection line to show changes in inflection line shape (one line is missing in the lower plot as the first simulation has no peaks in the inflection). Both the broad line and inflection line become wider for stronger hyperfine interactions.

Chapter 3.2.4.5 Simulated Effects of Two Magnetic Nuclei

This section will look at the effects of changing the hyperfine interactions between a charge carrier and a magnetic nucleus at site β with another magnetic nucleus at site α . The changes are similar to those seen in the previous section however not identical. The effect of changing the hyperfine interactions at site β are shown in Figure 3.13. For this case, the broad line increases in amplitude as the hyperfine interactions on site β become stronger, however the inflection line initially increases in amplitude, then decreases. These spectra were then normalized to the broad line and inflection line to see how the hyperfine interactions affect the shape and width of the lines. The normalized spectra are shown in Figure 3.14 with the spectra being normalized to the broad line in the top plot, and to the inflection line in the bottom plot. Both lines become broader as the hyperfine interactions are stronger however the effect is less pronounced than the previous case of only one site having a magnetic nucleus. Again, these values are unlikely to change during the course of a study unless a new defect is created (or an existing one is destroyed) due to stressing or charge injection.

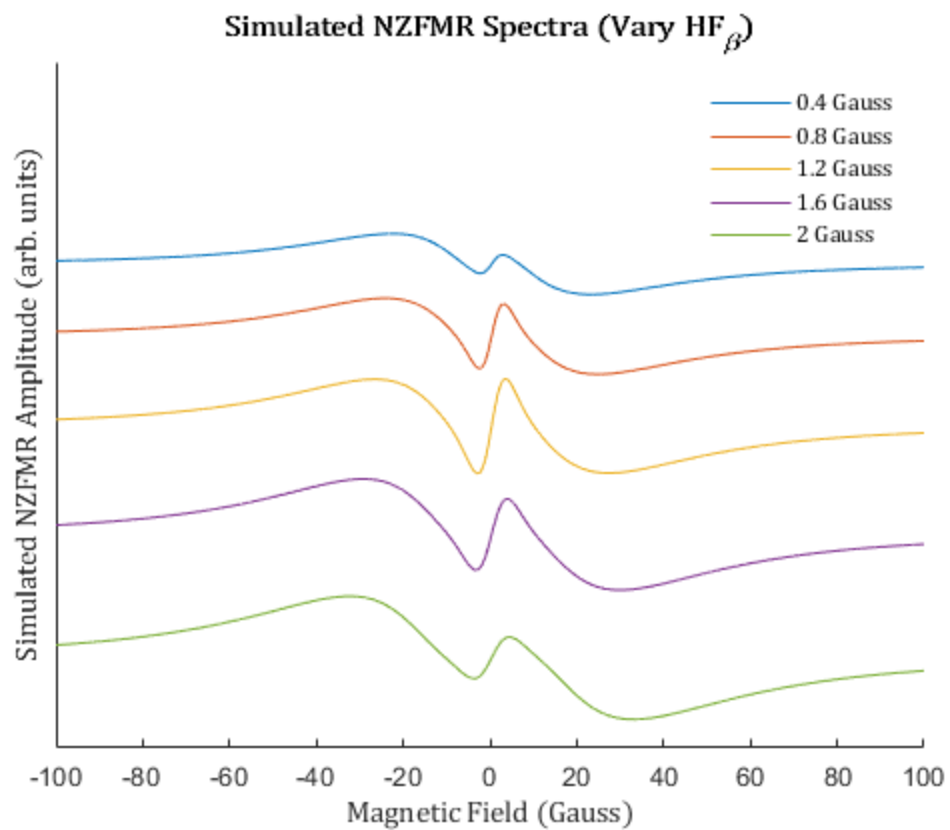


Figure 3.13: Raw simulated NZFMR spectra for different hyperfine values at site β with a magnetic nucleus at site α . The order shown in the legend matches the order of the plots.

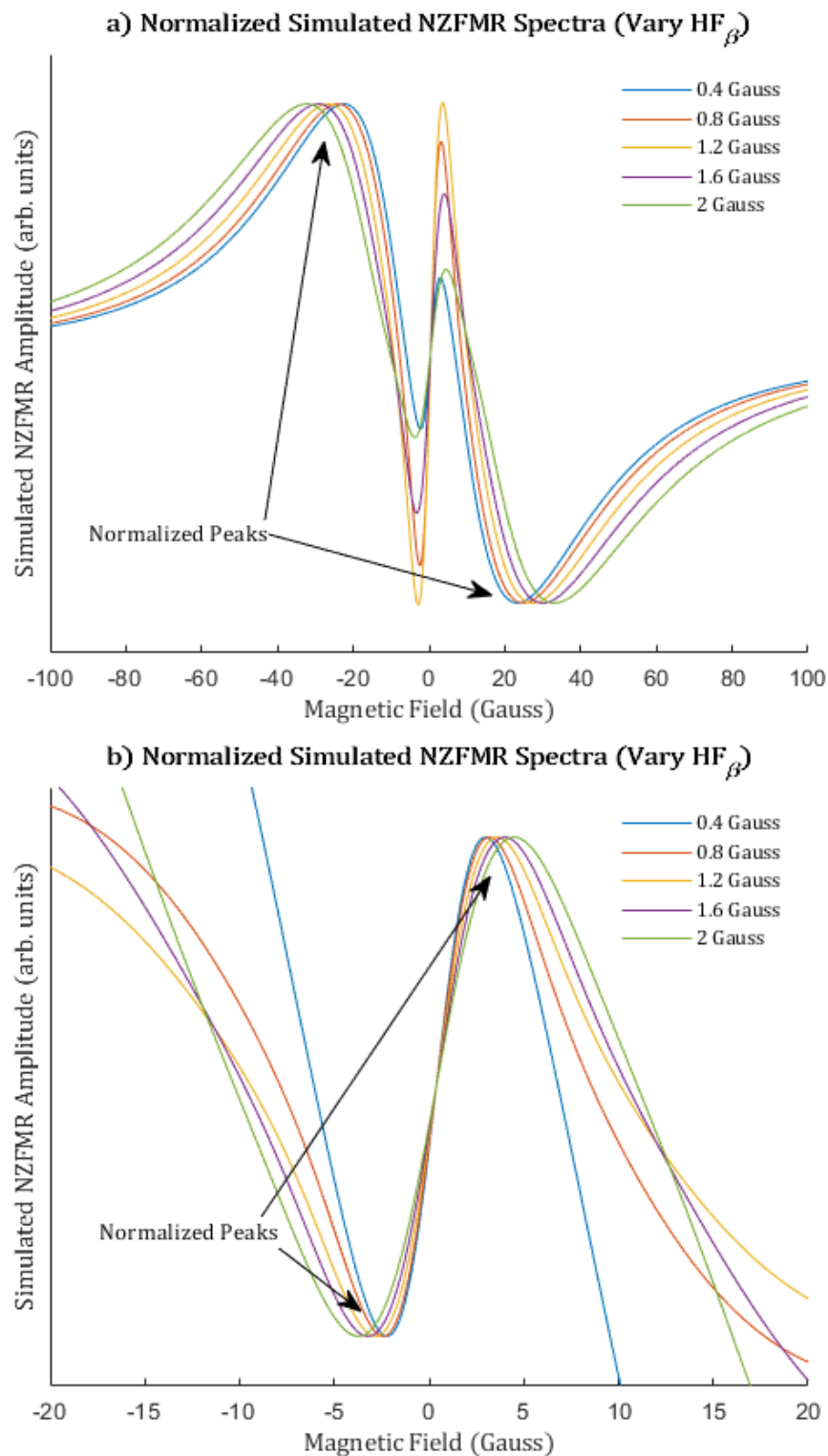


Figure 3.14: Normalized simulated spectra for different hyperfine values at site β with a magnetic nucleus at site α . a) Spectra normalized to the broader line to show changes in broad line shape. b) Spectra normalized to inflection line to show changes in inflection line shape. Both the broad line and inflection line become wider for stronger hyperfine interactions.

Chapter 4

Experimental Methods

The spectrometers utilized during the course of this study are described in this chapter. Each spectrometer will be given an identifying name which will be referred to when discussing experiments in this work. The breakdown of the spectrometers used includes two modified X-band EPR/EDMR spectrometers and two low-field EDMR/NZFMR spectrometers. One custom built wafer probing station spectrometer is utilized in appendix B however this will be discussed in greater length in that chapter.

Chapter 4.1 Bruker X-band EPR/EDMR Spectrometer

A modified commercial Bruker X-band EPR Spectrometer was utilized for some of the resonance measurements performed in this study. This spectrometer, which will be referred to as the “Bruker X-band spectrometer” consists of a commercial Bruker water cooled electromagnet and control system, Bruker 300 series X-band microwave bridge and plumbing, Bruker TE₁₀₄ X-band microwave cavity, Stanford Research Systems SR570 current to voltage pre-amplifier, Stanford Research Systems SR830 external lock-in amplifier, and computer for data acquisition with a National Instruments NI6259 data acquisition card and associated BNC 2110 DAQ connector block. Resonance measurements performed on this system utilized a modulation frequency of 12.5 kHz as it is the modulation frequency that provides the best signal to noise ratio in this spectrometer. The TE₁₀₄ cavity allows one to easily switch between resonance measurements on the sample and a known standard without removing anything from the cavity. A schematic diagram of this spectrometer is shown in Figure 4.1

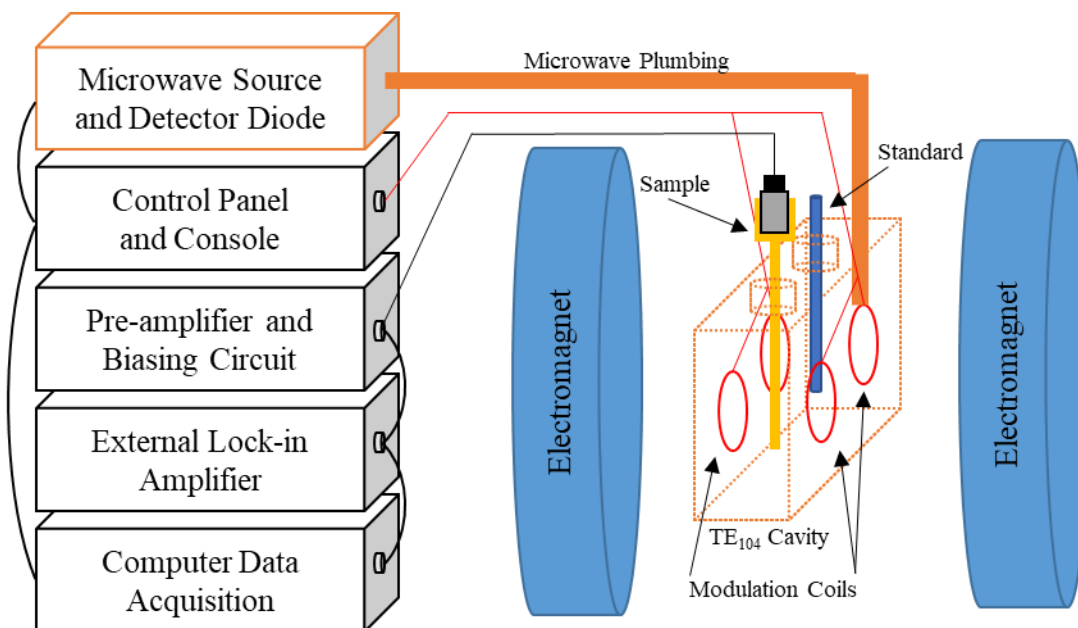


Figure 4.1: Cartoon schematic for Bruker X-band EDMR Spectrometer with TE_{104} microwave cavity.

Chapter 4.2 Lakeshore X-band EPR/EDMR Spectrometer

The second X-band spectrometer utilized in this study is a home-built system which shall be referred to as the “Lakeshore X-band spectrometer”. This spectrometer consisting of a Lakeshore water cooled electromagnet, a Lakeshore Cryotronics 450 temperature compensated Gaussmeter and Hall effect probe, a Micronow Systems microwave bridge with associated microwave plumbing and TE_{102} cavity, a Stanford Research Systems SR570 current to voltage pre-amplifier, and a computer for field control and data acquisition with a National Instruments PCIe-6374 data acquisition card and associated BNC 2110 DAQ connector block. Resonance measurements performed on this system could use any desired modulation frequency from near DC to approximately 20kHz. Modulation frequencies near 1 kHz were typically chosen. This system is capable of measuring the DC current in a sample during EDMR and NZFMR measurements. A cartoon schematic for the Lakeshore X-band is shown in Figure 4.2.

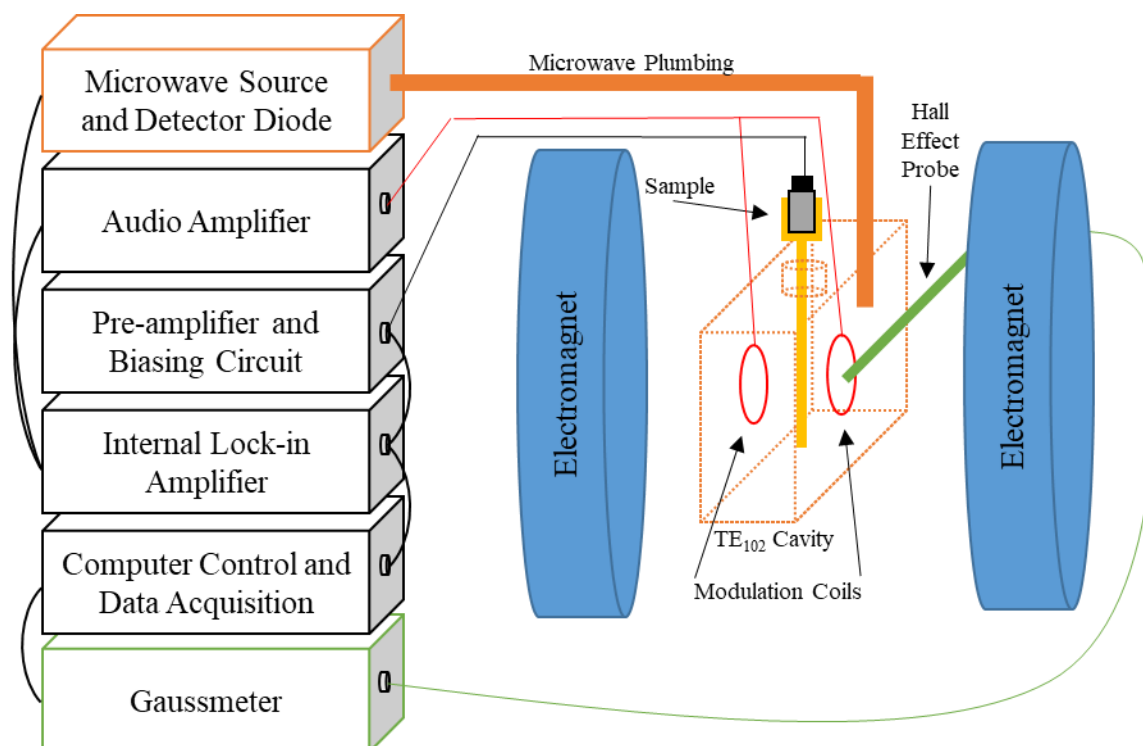


Figure 4.2: Schematic of Lakeshore X-band spectrometer with TE₁₀₂ microwave cavity.

Chapter 4.3 Home Built Kepco 100V 4A Low-Field EDMR/NZFMR Spectrometer

Some of the low-field EDMR and NZFMR measurements performed in this study were made on a home-built system which will be referred to as the “Kepco low-field/zero-field spectrometer” or “Kepco LF/ZF spectrometer”. This low-field EDMR and NZFMR spectrometer consists of a home-built nested Helmholtz coil electromagnet, a Kepco 400W 100V 4A Bipolar Power Supply, a Lakeshore Cryotronics 450 temperature compensated Gaussmeter and Hall effect probe, a Stanford Research Systems SR570 Current to Voltage Pre-amplifier, and a computer for field control and data acquisition with a National Instruments NI 6259 data acquisition card and associated BNC 2110 DAQ connector block. Resonance measurements performed on this system could use any desired modulation frequency from near DC to approximately 20kHz. Modulation frequencies near 1 kHz were typically chosen. The B_1 field

for the low field EDMR was provided by a DOTY 500MHz surface coil resonator with accompanying matching circuit. This system is capable of measuring the DC current in a sample during EDMR and NZFMR measurements. A schematic of the Kepco LF/ZF spectrometer is shown in Figure 4.3, adapted from Cochrane and Lenahan. [68]

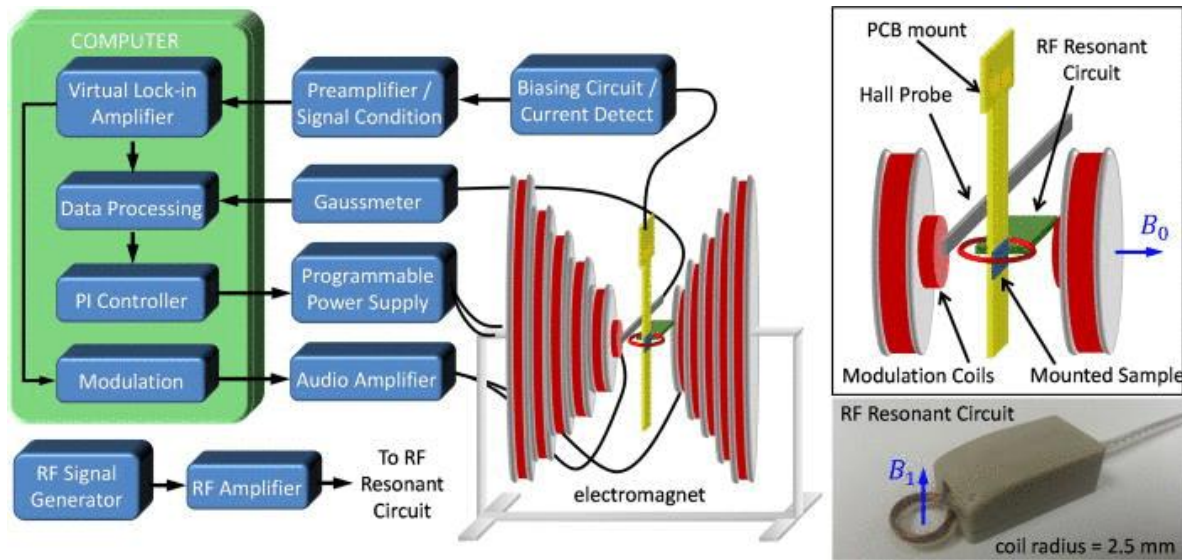


Figure 4.3: Schematic of Kepco LF/ZF spectrometer. Figure adapted from Cochrane and Lenahan. [68]

Chapter 4.4 Blue Spin, LLC Low Field EDMR/NZFMR Spectrometer

More low-field EDMR and NZFMR measurements performed in this study were made on a modified commercial Blue-Spin, LLC nested Helmholtz coil electromagnet and accompanying Blue-Spin electronics, computer, and data acquisition card, a Stanford Research Systems SR570 current to voltage preamplifier, SONY audio amplifier, and DOTY 350MHz surface coil resonator with accompanying matching circuit to provide the B_1 field for the low field EDMR. This spectrometer will be referred to as the “Blue Spin LF/ZF spectrometer”. The Blue Spin LF/ZF spectrometer is schematically very similar to the Kepco LF/ZF spectrometer in Figure 4.3.

Chapter 4.5 Other Equipment

Electrical measurements were made on other commercial testing equipment including an HP 4155 Semiconductor Parameter Analyzer and Boonton Electronics Model 72B capacitance meter. The Boonton capacitance meter will simply be referred to as the “capacitance meter”. A Kulicke and Soffa Model 4123 wire bonder was used to make electrical connections to the top contact of the samples. This process will be described as “wire bonding”.

Most samples were mounted onto custom made printed circuit board (PCB) “T’s” to make electrical contact while the sample is located inside the microwave cavities or low field electromagnets described previously. A USB connector is soldered to four contacts connected to parallel copper leads. Samples are bonded to a contact pad approximately four inches from the USB head using a conductive adhesive to create electrical contact between one lead and the back of the sample. The other three leads can then be wire bonded to bonding pads on the top of the sample to make electrical contact to the rest of the sample. A schematic of a “T” is shown in Figure 4.4. The sample and “T” are typically housed inside a quartz test tube to protect the sample from damage.

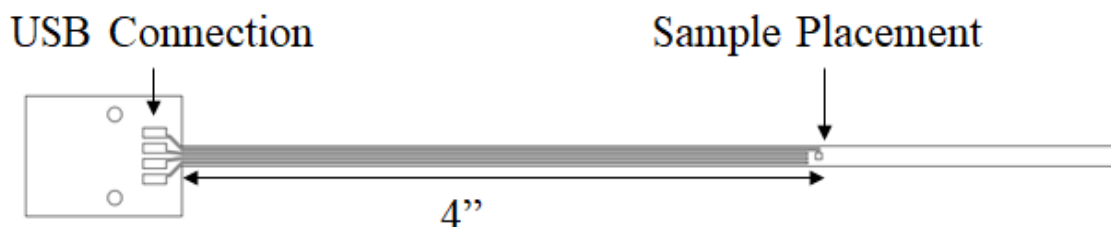


Figure 4.4: Schematic diagram of custom-made PCB "T" sample mount with copper leads. A USB connector is soldered to the 4 pads on the left side.

Chapter 5

Electrically Detected Magnetic Resonance and Near Zero Field Magneto-Resistance in Amorphous Carbon

SDTAT EDMR and NZFMR, along with other measurements, were performed on two types of amorphous carbon. The first of these samples were 500 nm amorphous hydrogenated carbon (a-C:H) hard mask film on p- silicon. The second was 1000 nm diamond-like (DLC/tetrahedral) carbon hard mask film on p- silicon. All amorphous carbon samples were grown using plasma enhanced chemical vapor deposition (PECVD) and have an aluminum/titanium top contact. The a-C:H samples are primarily sp^2 (triangularly) coordinated carbon with a hydrogen composition of 33% while the DLC samples are approximately half sp^2 coordinated and half sp^3 (tetrahedrally) coordinated carbon with a similar hydrogen content of 27%, there is only short and medium range order in these samples.

Atoms with sp^2 hybridized bonds have three nearest neighbors, with bond angles of 120 degrees in a planar triangle. Atoms with sp^3 hybridized bonds have four nearest neighbors, with bond angles of 109.5 degrees. Both of these bond angles can vary in materials due to strain and disorder. Illustrations of the sp^2 and sp^3 hybridized orbitals are shown in Figure 5.1.

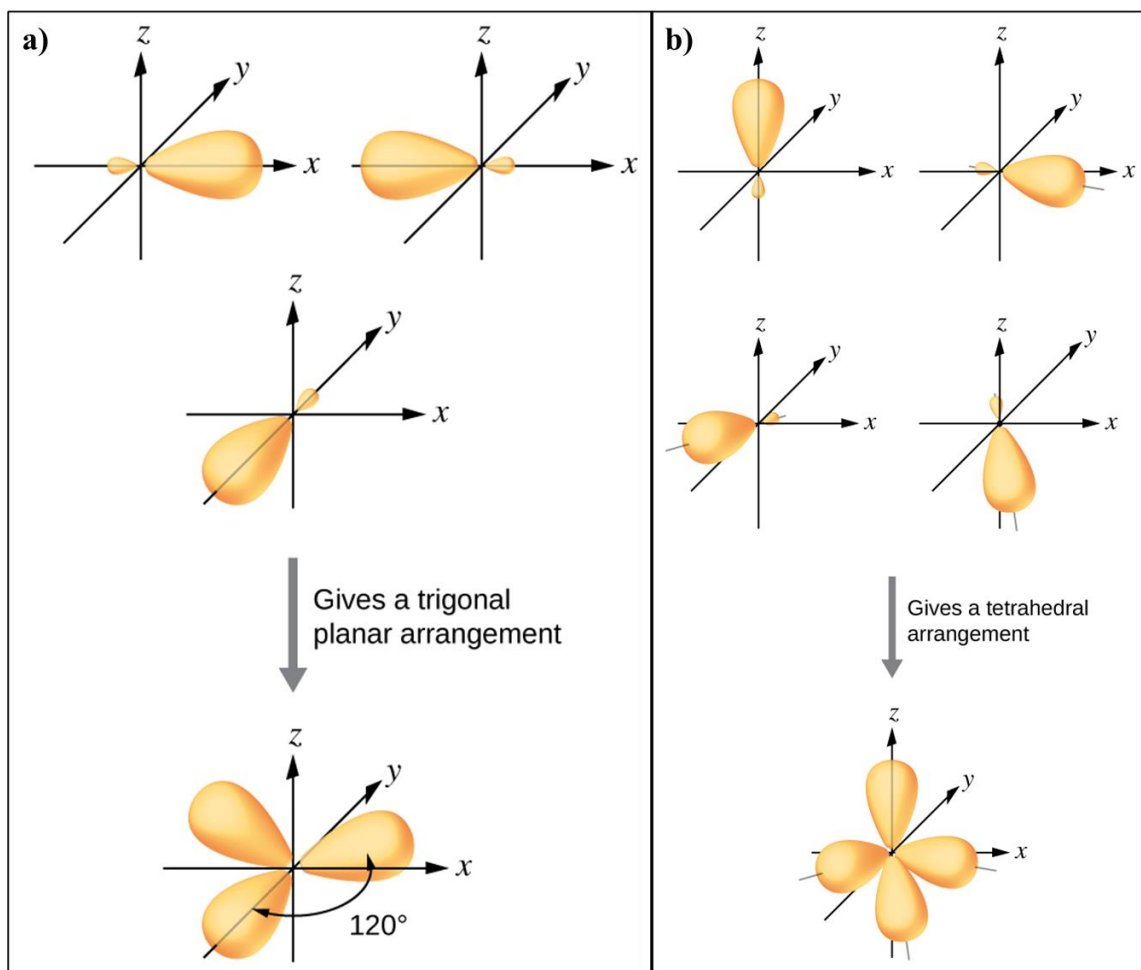


Figure 5.1: Diagrams of a) sp^2 hybridized orbitals with bond angles of 120 degrees and b) sp^3 hybridized orbitals with bond angles of 109.5 degrees. Adapted from [69].

Chapter 5.1 Defects and Electrical Conduction in Amorphous Carbon

The EDMR and NZFMR spectra measured in this work will be easier to understand with more knowledge of the known defects in these types of materials. Forms of amorphous carbon have been studied fairly extensively using EPR. [70]–[83] While a-C:H and DLC have different amounts of sp^2 and sp^3 coordination, the dangling bond defect in both materials occurs primarily on sp^2 sites because the sp^3 dangling bond tends to relax to sp^2 configuration. [70], [72], [84]

The small atomic size of carbon also leads to very little spin-orbit coupling, causing most defects

in amorphous carbon to have g values between 2.0024-2.0029 [71]–[82] although some diamond-like carbon samples have resonance spectra with g values as high as 2.0047. [71], [83] Paramagnetic impurities can also cause higher g values at approximately 2.0053. [71] We expect to observe spectra with zero-crossing g values in the range of 2.0024 to 2.0047. Defect states in amorphous carbon samples have been linked to π orbitals and found in a continuous distribution throughout the bandgap. [70], [84]

Chapter 5.2 EDMR and NZFMR in 500 nm Thick Amorphous Carbon:

SDTAT EDMR and NZFMR as well as other measurements were conducted on 500 nm amorphous hydrogenated carbon on p- silicon capacitor dots. The a-C:H was deposited via PECVD and the top contact is 2mm^2 , composed of approximately 100nm of titanium with approximately $1\mu\text{m}$ of aluminum on top. The composition of the carbon layer is 58% carbon, 33% hydrogen, 7% oxygen, and 1% nitrogen. The structure of the a-C:H is shown in Figure 5.2.

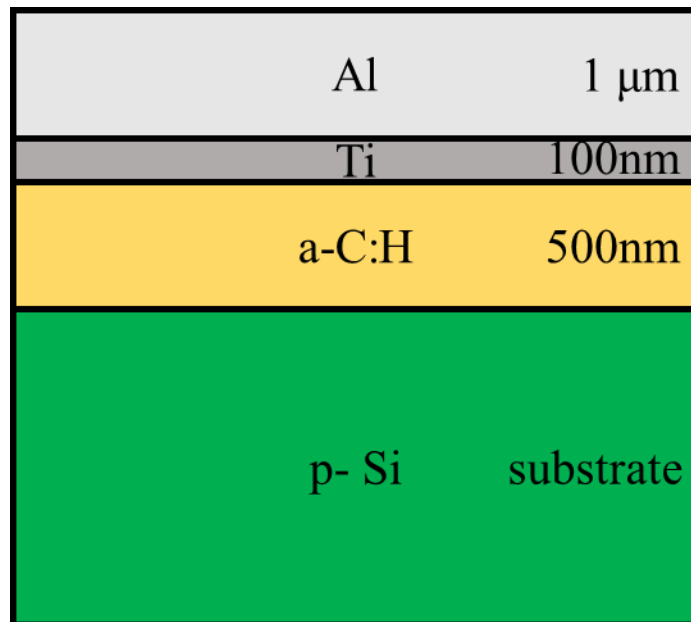


Figure 5.2: Schematic illustration of 500 nm a-C:H samples.

Samples were mounted on custom made USB connected PCB “Ts”, with the back contact connected to a bonding pad via electrically conductive paint. Electrical connection to the top contact was made via wire bonding. The samples were initially electrically characterized using capacitance vs voltage measurements conducted using the semiconductor parameter analyzer and capacitance meter. Some initial current vs voltage measurements were made using the semiconductor parameter analyzer, however, the current in these samples is not stable and decreases rapidly with time. The rate at which the trap assisted tunneling current drops in the samples is larger for larger magnitude biases, and a negative bias has a larger effect than a positive bias.

Chapter 5.2.1 X-band EDMR in 500 nm a-C:H

SDTAT EDMR measurements were made on 500 nm a-C:H in order to help identify the defects involved in the electronic transport in the material. The measurements were made on two X-band EDMR spectrometers. An X-band SDTAT EDMR spectrum from these samples, measured in the home-built Lakeshore X-band spectrometer, is shown in Figure 5.3. This measurement was performed with the sample biased at +4V on the top contact of the capacitor dot with a field modulation amplitude of 5 Gauss at 1150 Hz. The zero-crossing g value of the defect, 2.0022, was determined by comparing the measured spectra to a known standard.

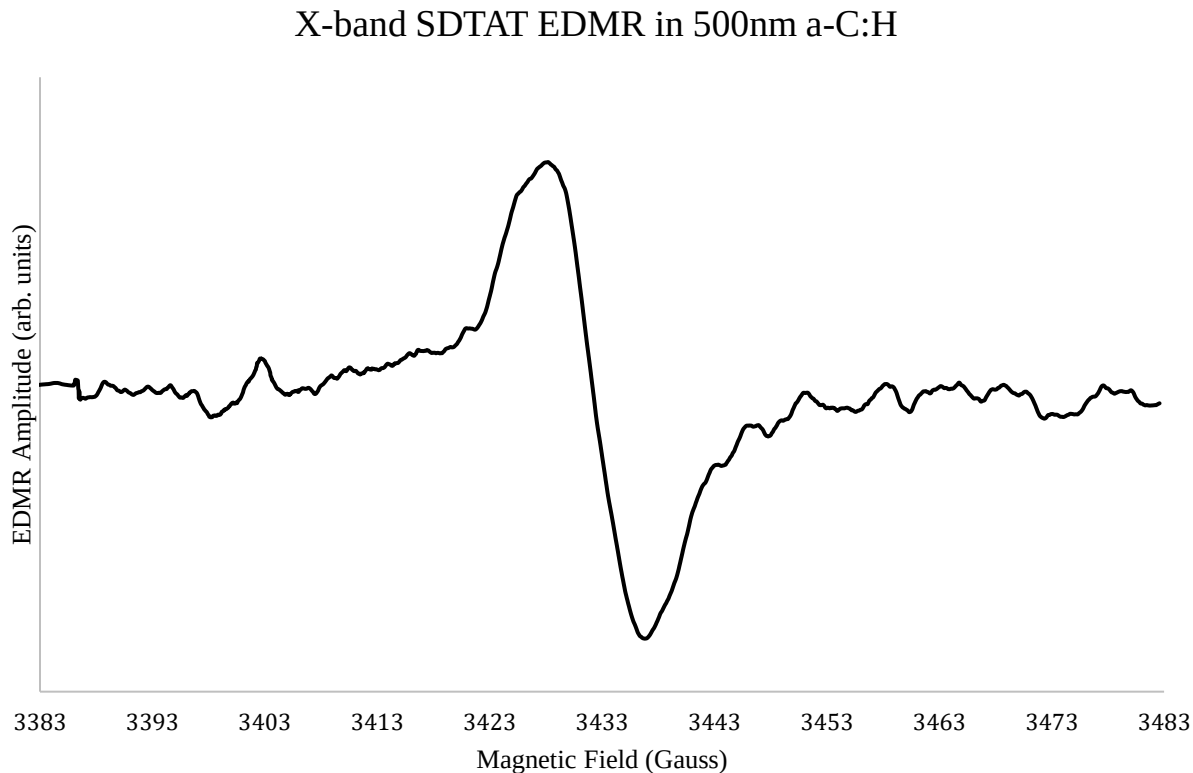


Figure 5.3: X-band SDTAT EDMR in 500nm amorphous carbon on Si. Applied bias of +4V. The signal width is 9.1 Gauss with a zero-crossing g value of 2.0022.

The measurement resulted in a 9.0 Gauss wide spectrum with a zero-crossing g value of 2.0022, which is very close to, and within experimental error of, the free electron g of 2.0023..., suggesting that there is very little spin-orbit coupling in the sample. This result makes sense when we consider the elements present in the sample. The sample is composed primarily of the small elements, carbon and hydrogen, which as discussed in chapter 2.1.3.1 will have very little spin orbit coupling. This defect is likely a carbon dangling bond, as there are no other atomic nuclei present in a high enough concentration that can have a dangling bond in the material, and the measured g -value aligns with the expected values discussed in chapter 5.1. Electrons likely hop from site to site across the material through these dangling bond defects.

X-band SDTAT EDMR was performed on a similar sample under negative bias using the Bruker X-band spectrometer. The sample was biased at a constant -3V and a magnetic field modulation of 5 Gauss at 12.5kHz was used. The increased modulation frequency was utilized to improve the signal to noise ratio on the spectrometer. The results are shown in Figure 5.4. The signal amplitude decreased rapidly over time and a representative set of spectra over approximately 30 minutes of measurements (1 minute per trace) are shown as individual scans without averaging. The zero-crossing g value of the spectra measured under negative bias is 2.0028, within the expected range of g values for sp^2 coordinated carbon dangling bonds.[71] The lines are all 9 Gauss wide, the same as the line width under positive bias. The defects giving rise to these spectra at both positive and negative bias are likely the same carbon dangling bond.

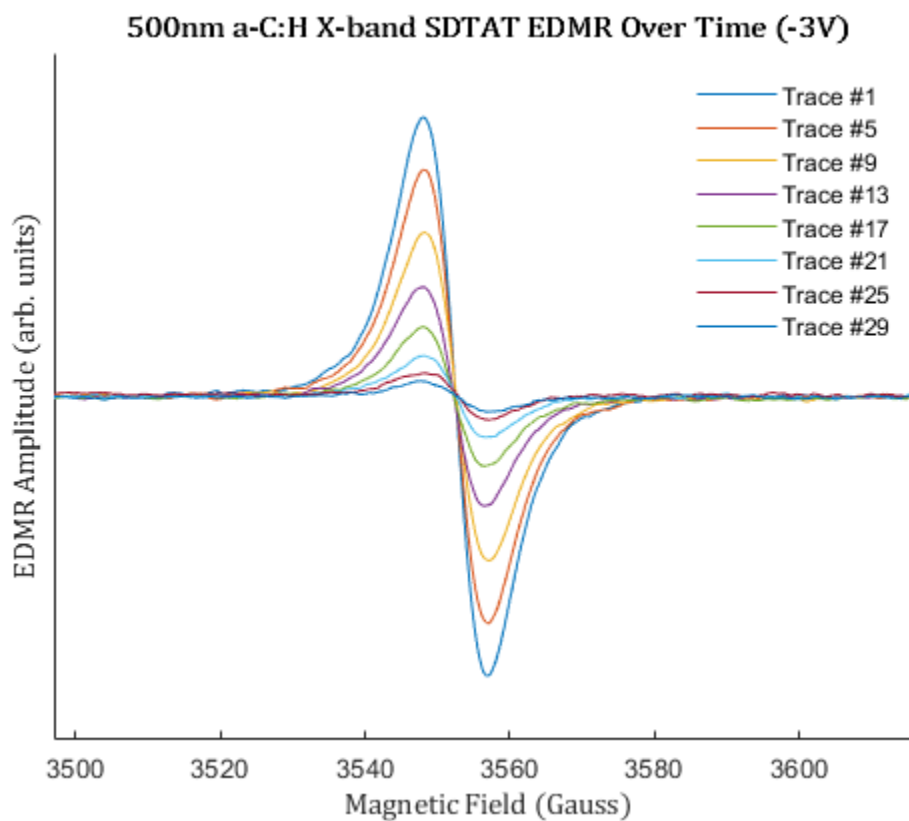


Figure 5.4: X-band SDTAT EDMR in 500nm a-C:H over time under constant applied bias of -3V. The signal amplitude decreases rapidly with time. Each trace takes approximately 1 minute to complete.

Typically, signal averaging is utilized in EDMR and NZFMR measurements in order to improve the signal to noise ratio of the measurement. The signal averaging technique requires that the DC current in the sample and the measured spectrum stay relatively consistent over the period of measurement, typically hours to days. The a-C:H samples do not exhibit such stable behavior as both the DC current through the sample and the amplitude of the measured spectra change rapidly with time. Fortunately, the signal to noise ratio of the measured spectra are large enough to not require signal averaging. The reduction in DC current over time is discussed in more detail in Chapter 5.2.2.

The amplitude of the measured spectra decreases rapidly over time until it levels off after prolonged applied bias. This effect occurs when the sample is under negative bias, and very little change is observed in samples in which only a positive bias is applied. The amplitude of the measured SDTAT EDMR spectra over time is shown in Figure 5.5.

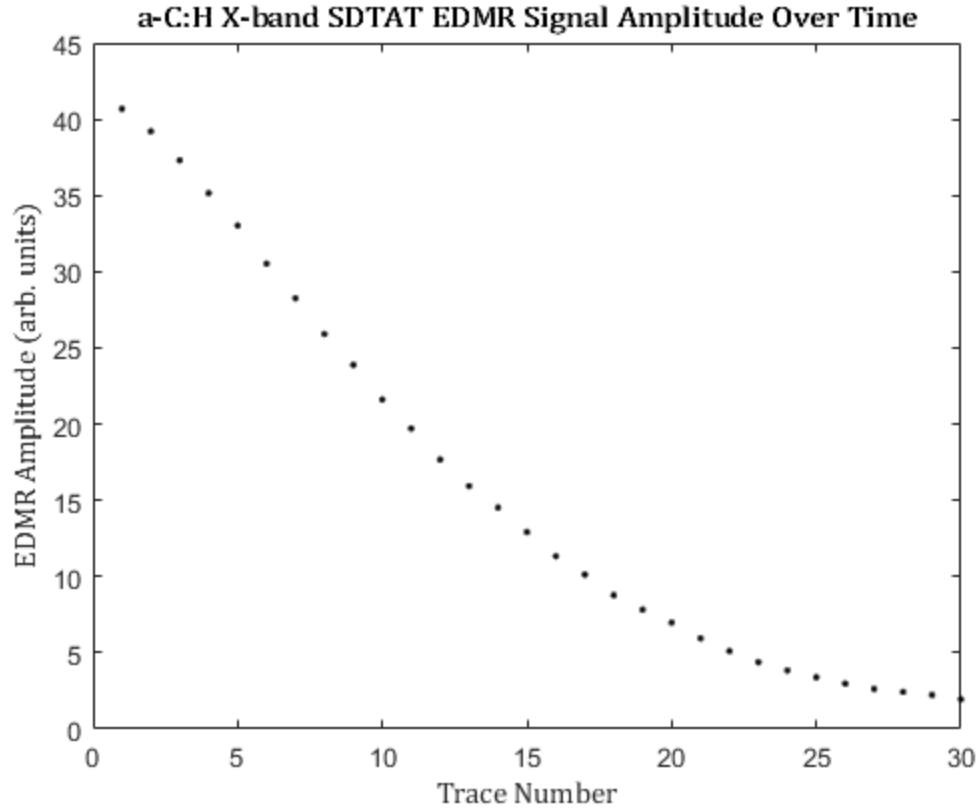


Figure 5.5: Amplitude of measured SDTAT EDMR spectra in 500nm a-C:H over time. The amplitude of the measured spectra decreases rapidly at first, then levels off after a prolonged period of time.

Although the signal amplitude decreases over time at negative bias, the shape and linewidth of the signal do not change. Normalized spectra are shown in Figure 5.6 in which the shape of the line is unchanged, indicating that the same defect is responsible for conduction through the material and there is little or now change in the types of defects involved in leakage current during the stressing.

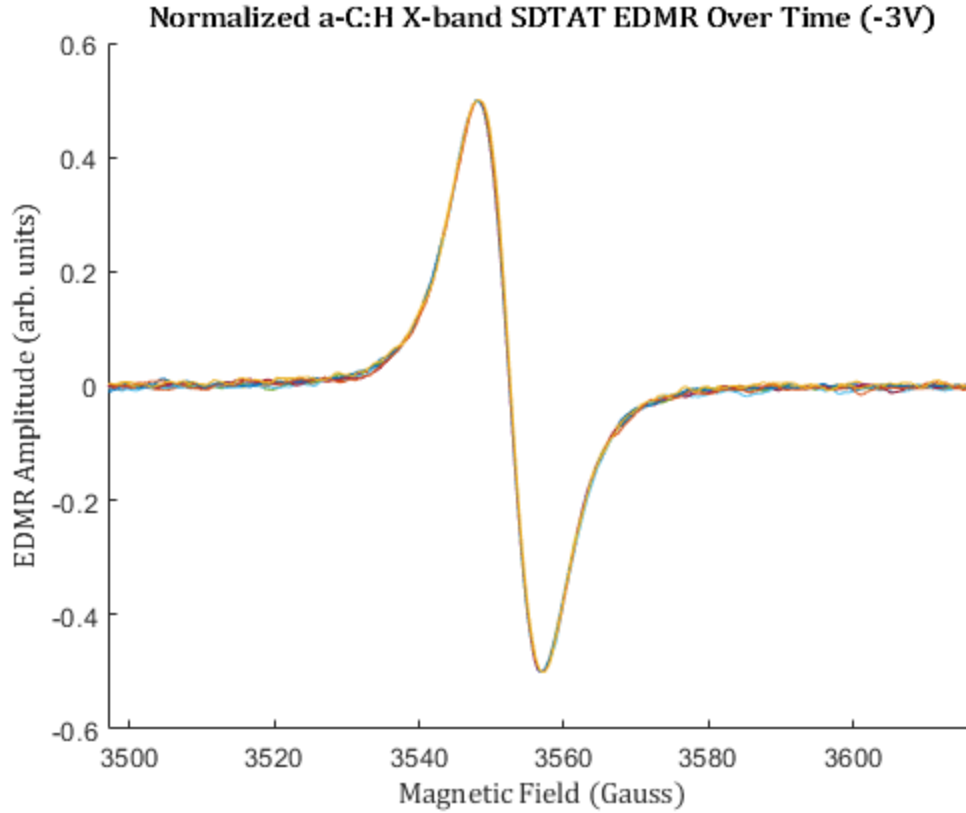


Figure 5.6: Normalized SDTAT EDMR in 500nm a-C:H over time. The signal shape and linewidth do not change over approximately 30 minutes.

Chapter 5.2.2 NZFMR and Low Field EDMR in 500 nm a-C:H

After performing X-band SDTAT EDMR on these samples, SDTAT NZFMR and low field EDMR measurements were performed on fresh samples. These measurements were made on the Kepco LF/ZF spectrometer because DC current can be measured while performing EDMR and NZFMR. Some of the NZFMR results from these samples are shown in Figure 5.7. These measurements were made with a magnetic field modulation of 1 Gauss at a frequency of 1000 Hz. The device was biased at -5V on the top contact. The signal amplitude decreases in the same way that the X-band EDMR signal did.

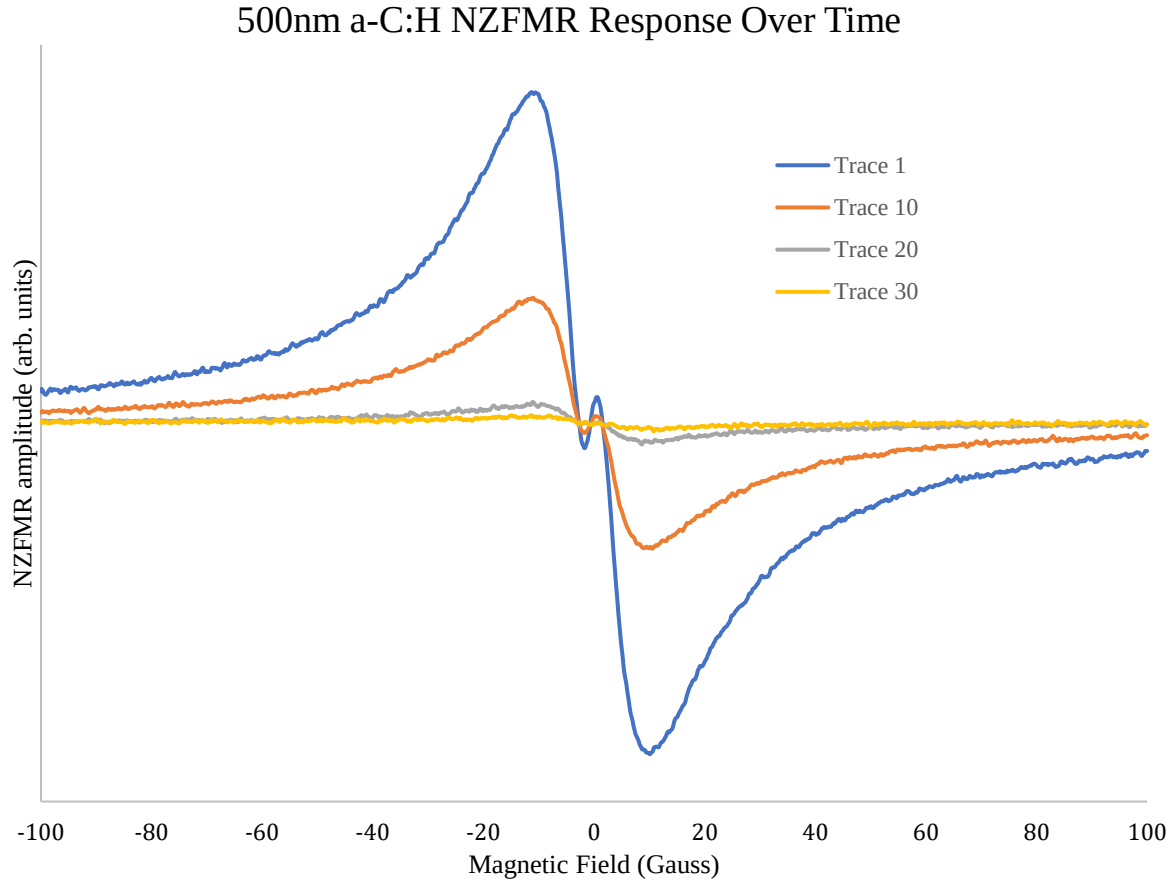


Figure 5.7: SDTAT NZFMR response in 500 nm amorphous carbon over time. Each trace takes approximately 10 minutes to measure. The signal amplitude decreases over time but remains 21 Gauss wide. Signal amplitude is not normalized. Measurements were made using a 1 Gauss modulation amplitude at 1kHz. Sample biased at -5V.

The high signal to noise ratio and accurate line-shape of these signals make them good candidates to analyze in terms of the stochastic Liouville equation described in chapter 3. As stated previously, the defects involved in conduction are likely carbon dangling bonds. The hyperfine interactions in this particular material likely arises from nearby hydrogen nuclei, as they are the only magnetic species in the sample in high enough concentration to be relevant. Only 1.1% of the carbon nuclei possess a magnetic nucleus, whereas nearly 100% of the hydrogen nuclei are magnetic. Recall that the hydrogen content in these films is very high, about

33%. A simulated spectrum was fitted to the 21 Gauss wide experimental spectrum. The simulated and measured spectra are shown in Figure 5.8.

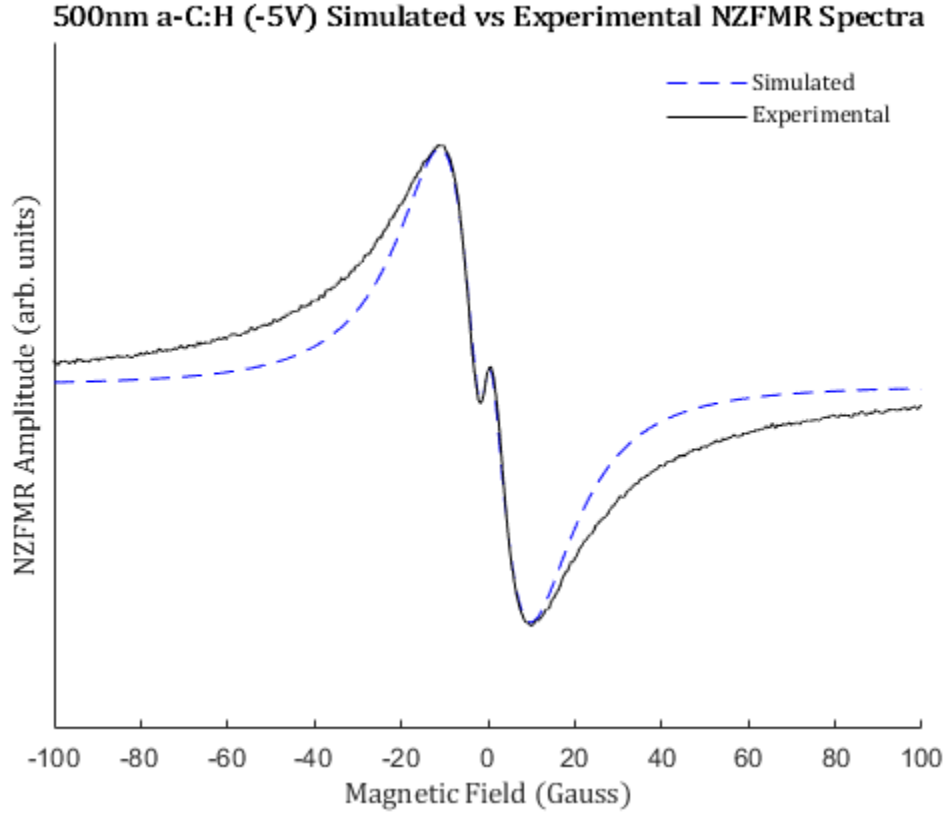


Figure 5.8: Simulated and measured NZFMR spectra in 500nm a-C:H. The measured spectrum is the largest of the spectra shown in the previous data set. The simulated spectrum utilizes values of $r_{e\alpha} = 530 \pm 25 \text{ GHz}$, $r_{ae} = 97 \pm 10 \text{ MHz}$, $r_{\alpha\beta} = 340 \pm 50 \text{ MHz}$, and hyperfine coupling constants on both sites of $3.4 \pm 0.5 \text{ Gauss}$.

The simulated spectrum was fit using a least squares method outlined by Frantz et al. [64]. The resulting hyperfine coupling constants for sites α and β were both found to be approximately $3.4 \pm 0.5 \text{ Gauss}$, as reasonable fits could be made using coupling constants within approximately 0.5 Gauss . This is considered a hop from a site with a nearby hydrogen to another site with a nearby hydrogen. The resulting generation rate from the fit, $r_{e\alpha}$, was approximately $530 \pm 25 \text{ GHz}$, while the resulting dissociation rate from the fit, r_{ae} , was approximately $97 \pm 10 \text{ MHz}$. The

resulting singlet probability of hopping rate, $r_{\alpha\beta}$, was approximately 340 ± 50 MHz. This fitting algorithm was constructed to consider the contribution from a single species, assumed to be hydrogen because its concentration of magnetic nuclei was 2 orders of magnitude higher than that of carbon in this film.

These values appear to be reasonable for this sample, indicating that the computational model, though not perfect, is a useful analytical tool that can be used to extract certain parameters from NZFMR spectra. The value of the hyperfine coupling constant is physically plausible. It must be a value between the magnetic field due to a nearby hydrogen nucleus at a distance of a few angstroms (approximately 1 Gauss) and the low-field EDMR linewidth (approximately 7 Gauss). The linewidth in low-field EDMR measurements is dominated by hyperfine interactions and a hyperfine coupling constant greater than 7 Gauss in this sample would result in a wider low-field EDMR line. A hopping rate larger than the dissociation rate is also plausible as the current is dominated by variable range hopping events.

Current through the sample dropped significantly during the measurement along with the signal amplitude. The drop in the steady state DC current over time is shown in Figure 5.9.

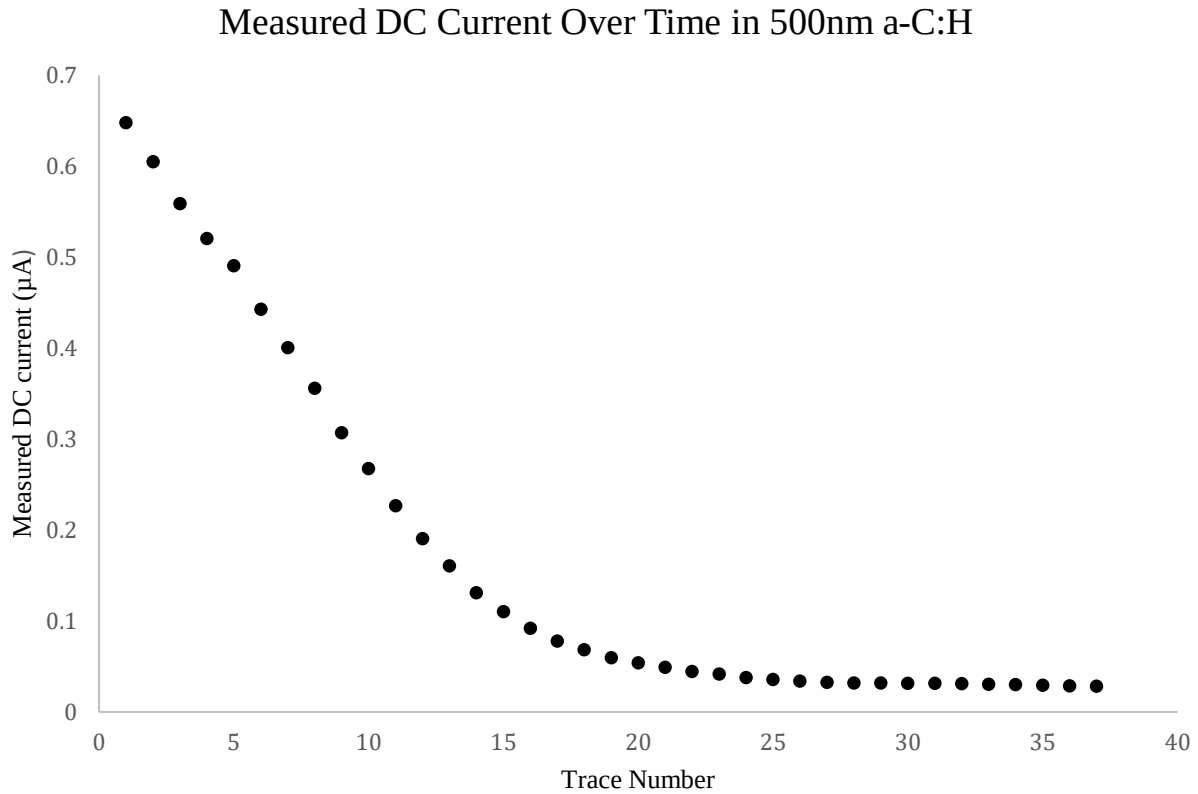


Figure 5.9: DC current over time in 500nm a-C:H under constant -5V bias during NZFMR measurement.

While both the DC current and the NZFMR signal amplitude both decrease over time, the NZFMR signal amplitude decreases faster, with the percent change of the current due to NZFMR decreasing over time under a constant bias. This is shown in Figure 5.10.

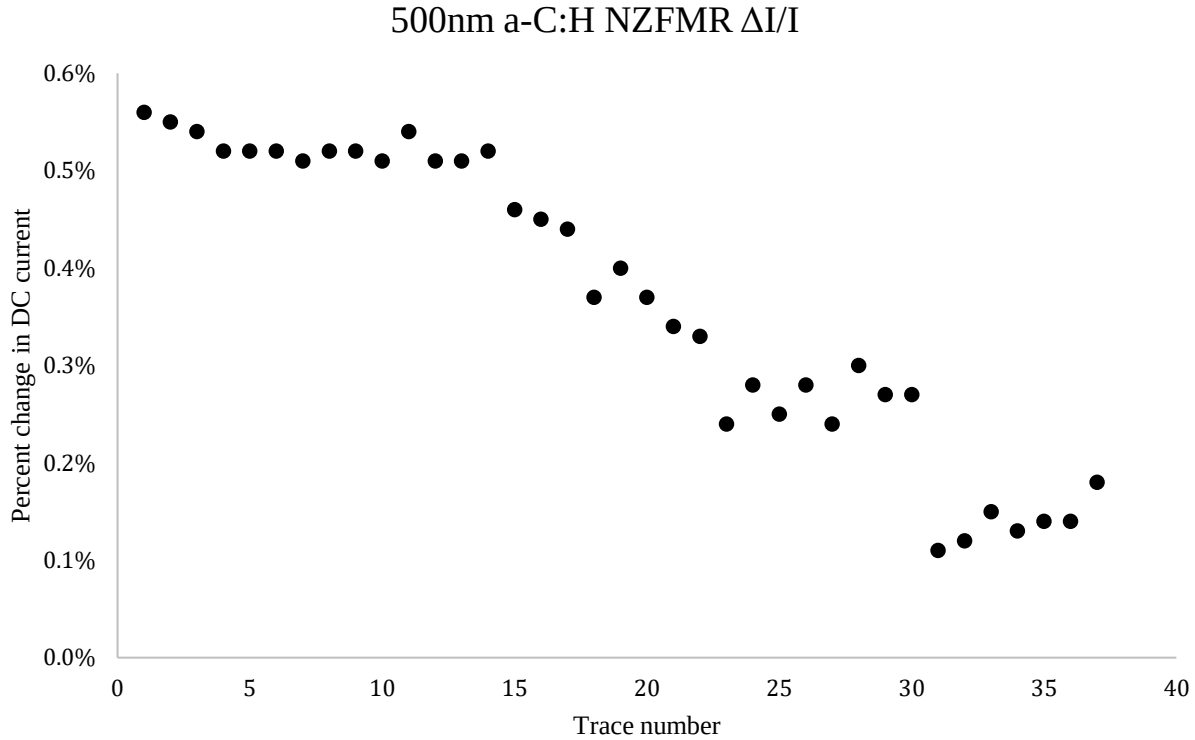
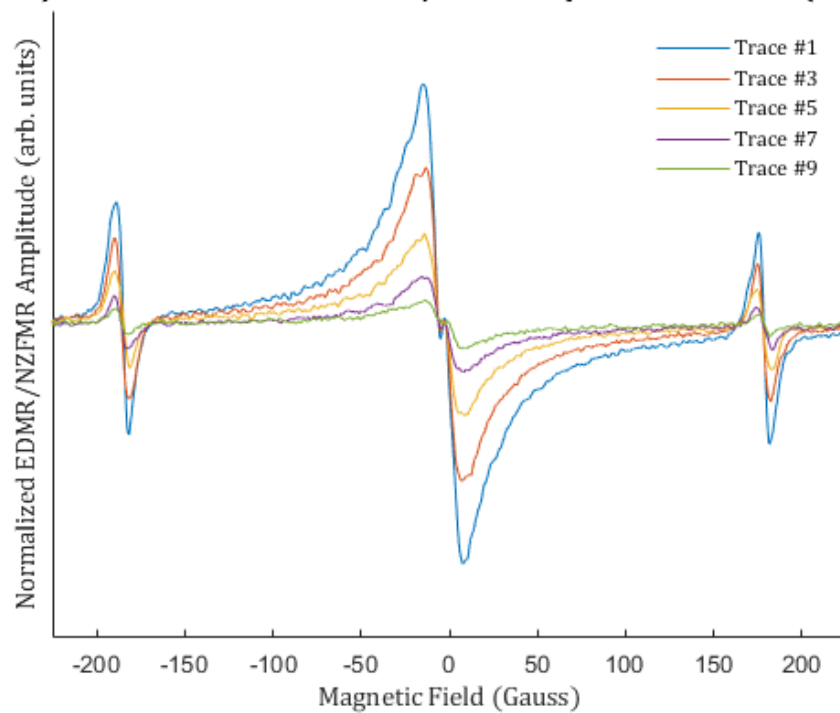


Figure 5.10: Percent change in current due to NZFMR response during measurement under constant -5V bias.

Further studies on these samples showed that the current through the device would decrease monotonically when under negative bias until it stabilized at a lower value which could be two orders of magnitude smaller than the initial current. During this change in current and signal amplitude under a constant bias, there is no discernable change to the line shape or line width of the signals. The reduction in amplitude is shown in Figure 5.11 a) which depicts both the NZFMR and low-field EDMR response over time under a constant -4V bias. The constant shape is shown in Figure 5.11 b) with the normalized spectra. The current in this measurement decreases like in Figure 5.9, with a starting current of approximately 10 μA at the moment the bias was applied. This current dropped to approximately 500 nA after 20 minutes under constant bias. For these measurements, each trace took approximately 2 minutes to complete.

a) 500nm a-C:H SDTAT NZFMR/EDMR Amplitude over Time (-4V)



b) a-C:H Normalized SDTAT NZFMR/EDMR Amplitude over Time (-4V)

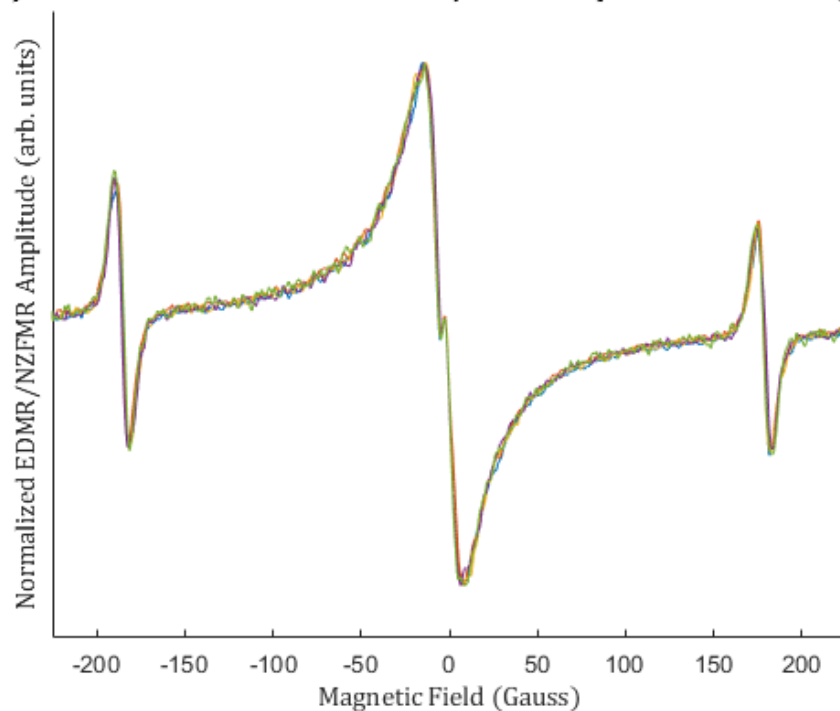


Figure 5.11: a) Change in NZFMR and EDMR amplitude over time under constant -4V bias during measurement. b) Normalized traces from a) showing no discernable change in the shape or linewidth over time, the smaller signals have reduced SNR. The legend applies to both parts of the figure.

The line shape in these measurements, with both low-field EDMR and NZFMR, does not change over time. This would suggest that, like in the pure NZFMR measurement, only the generation rate at which charge carriers enters the material, r_{ea} , is changing. The low-field EDMR linewidth is 7.5 Gauss wide, which is somewhat smaller than the 9 Gauss wide X-band EDMR linewidth.

The DC current through the sample initially recovers slightly when subjected to positive bias until dropping again after a short period of time. The measured current through the sample is shown in Figure 5.12. The percent change in current due to NZFMR also increases during this recovery period, doubling over approximately 10 minutes then somewhat stabilizing, when subjected to a constant +4V bias. This is shown in Figure 5.13.

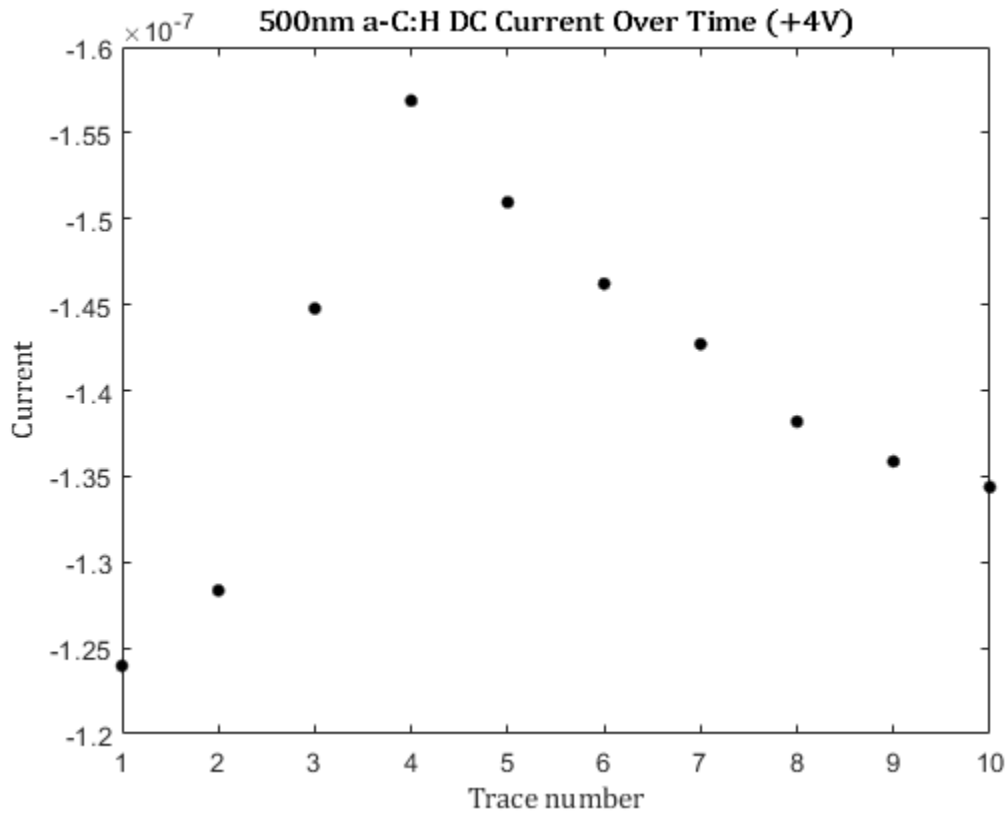


Figure 5.12: Measured DC current in 500nm a-C:H sample over time under constant +4V bias. This measurement was taken after the measurement at a -4V bias shown in Figure 5.11.

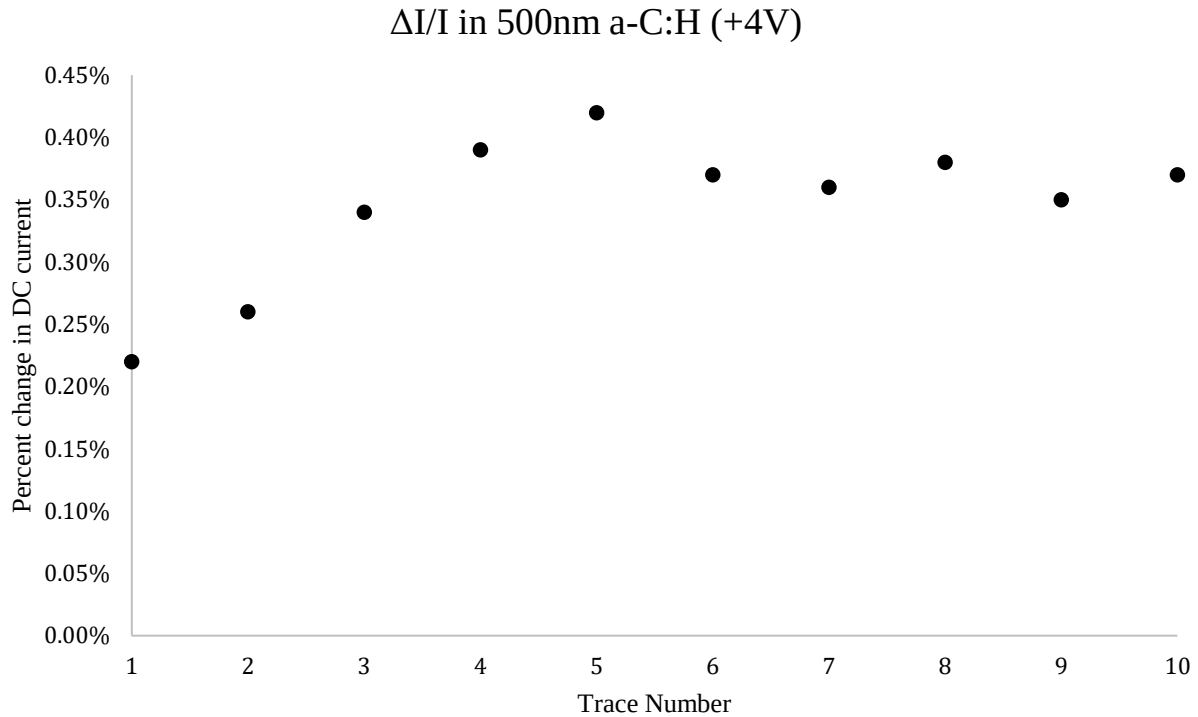


Figure 5.13: Percent change in current due to NZFMR over time under constant bias of +4V.

After a series of biases over a prolonged period of time, the applied bias must be increased in order to measure an NZFMR/EDMR spectrum. After applying a bias of -8V, a DC current of 280 nA is initially measured, much less than the 10 μ A measured as soon as the initial -4V was applied for the previous measurements. This current dropped to approximately 118 nA indicating that the relative decrease in current is reduced the longer the device is under an applied bias.

Capacitance vs voltage measurements were made on the sample between some NZFMR measurements and are shown in Figure 5.14. These measurements show a leftward shift after negative bias, and a small rightward shift after positive bias. This indicates that there is positive space charge accumulating in the insulating material when under negative bias, and positive

space charge leaves the insulating material under positive bias. It is also clear to see the effect of time on the amount of space charge in carbon film. Each of the measurements in Figure 5.14 was made sequentially and stressing occurred during NZFMR/EDMR measurements. There is a large leftward shift (approximately 3V) between the measurement made on the fresh sample and the measurement made after the initial -4V bias over 10 minutes. An additional 8 hours biased at a constant -4V shows a much smaller leftward shift. A small rightward shift in the plot is shown after the same sample is biased at +4V for a period of 20 minutes. Finally, there is a large leftward shift in the plot after being biased at -8V for approximately 20 minutes.

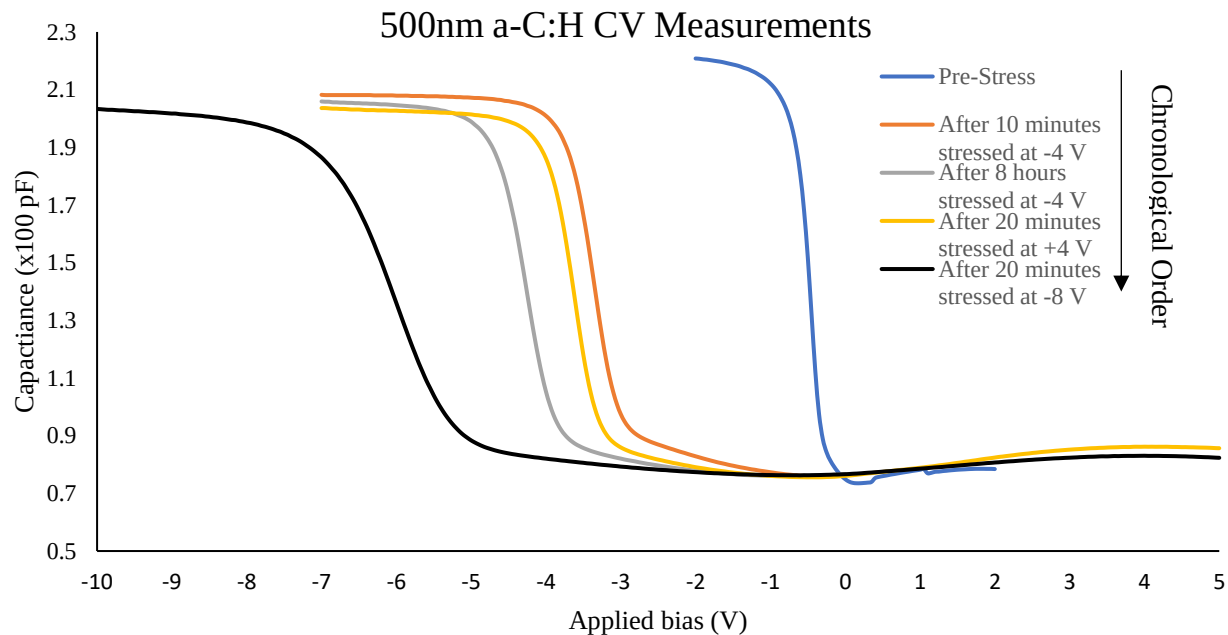


Figure 5.14: Capacitance vs voltage measurements made on 500nm amorphous carbon on Si MOS capacitors after EDMR and NZFMR measurements. The measurements were made in the order shown. The sample was first biased at -4V for approximately 10 minutes, then at -4V for approximately 8 hours, then at +4V for approximately 20 minutes, then at -8V for approximately 20 minutes. Capacitance vs voltage measurements were made between EDMR/NZFMR experiments. The shift in the curve to the left indicates positive space charge in the insulating layer. A 1-volt shift left corresponds to approximately 6×10^{10} charges cm^{-2} .

The leftward shift in the capacitance vs voltage plots in Figure 5.14 corresponds to approximately 6×10^{10} charges cm^{-2} per volt. The slight downward shift in the accumulation capacitance between the pre-stress and post-stressed measurements is likely due to the rapidly changing electrical conductivity of the sample and relatively large current through the sample during the initial measurement. Both of these effects have been observed to cause the capacitance meter to measure slightly different values in other samples. There does not appear to be a way to make a more accurate initial measurement as the biasing used in the measurement causes the change in the sample, therefore a second, more stable measurement would yield different results. The accumulation and inversion capacitances do not change once the sample is biased long enough to become more stable throughout the rest of the measurements made.

Approximate band diagrams for the a-C:H samples with different levels of fixed space charge in the carbon layer are shown in Figure 5.15. Band diagrams were modeled using the Boise State University College of Engineering Multi-Dielectric Energy Band Diagram Program version 3.1.6. The space charge in the a-C:H is modeled using 2-D sheet charge as the program's fixed charge modeling capabilities are limited to 2-D sheet charge. Band alignment and energy level offsets were determined using data from Robertson [72], [85] and Schäfer et al. [86]. It is clear in the modeled band diagrams how positive space charge in the carbon would raise the tunneling barrier that holes experience, thereby reducing the tunneling current. These models show how the reduction in current seen in the a-C:H samples can be related to the larger barrier due to positive space charge observed in the capacitance vs voltage measurements.

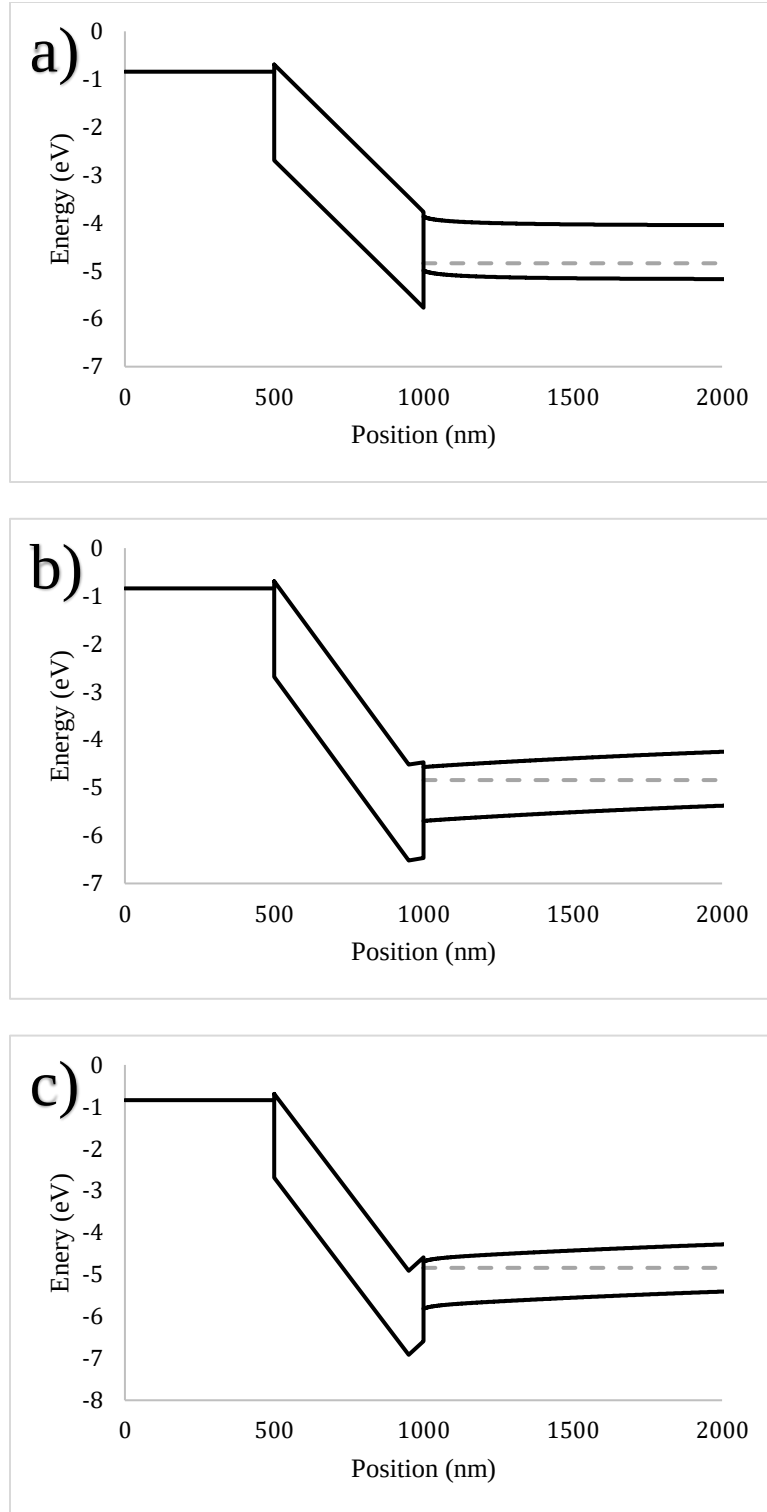


Figure 5.15: Band diagrams of the Ti/a-C:H/p- Si samples under bias of -4 V for a) no space charge in the a-C:H, b) 2×10^{11} positive charges cm^{-2} positioned 50nm from the C/Si interface, and c) 4×10^{11} positive charges cm^{-2} positioned 50nm from the C/Si interface.

The largest bias applied to these samples was -60V after a series of smaller biases. The sample showed the same monotonic decrease in DC current and NZFMR/EDMR amplitude over time during this measurement. The DC current started at 1 μA , once again smaller than the 10 μA measured immediately after applying the initial -4V bias. The DC current dropped to 200 nA under the constant -60V bias. No bias larger than 60V was used in order to prevent damage to the electronic components of the spectrometer. The averaged spectra measured under a bias of -60V can be seen in Figure 5.16.

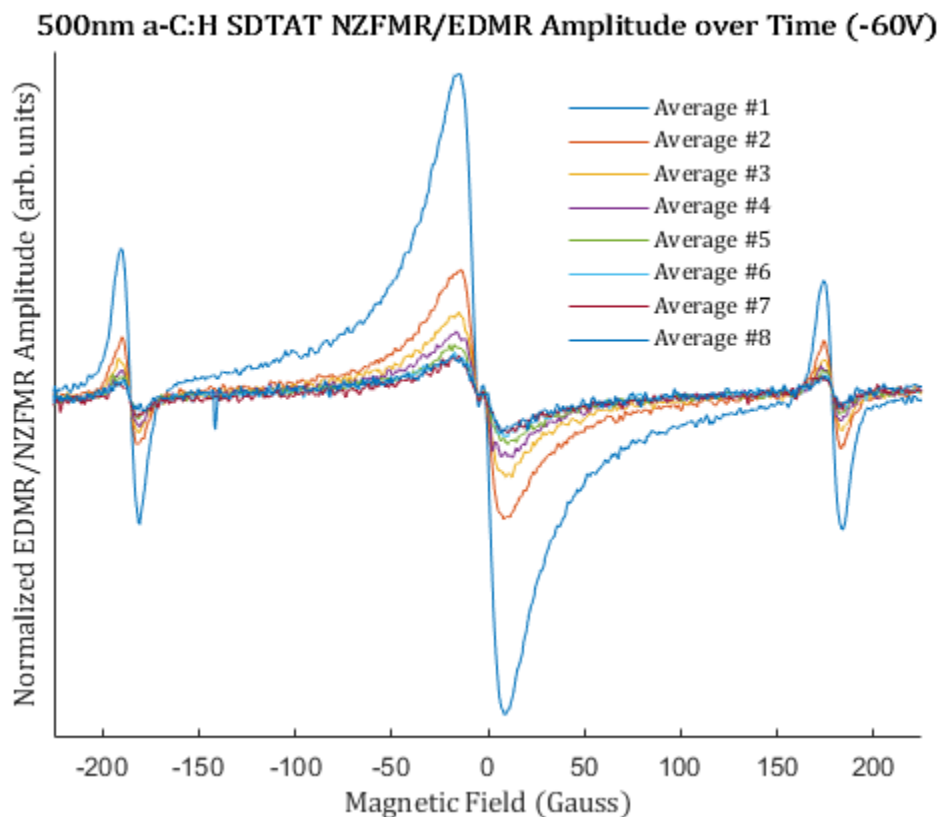


Figure 5.16: SDTAT NZFMR and EDMR in 500nm a-C:H under -60V bias over time.

There was no discernable change in the shape of either the EDMR or NZFMR lines even at this very large bias of -60V. Comparing the shape of the both the EDMR and NZFMR lines

for multiple biases shows a similar trend. Even for different biases, the line shapes do not change, only the signal amplitude drops as the DC current through the sample also drops.

Normalized spectra for different biasing conditions is shown in Figure 5.17.

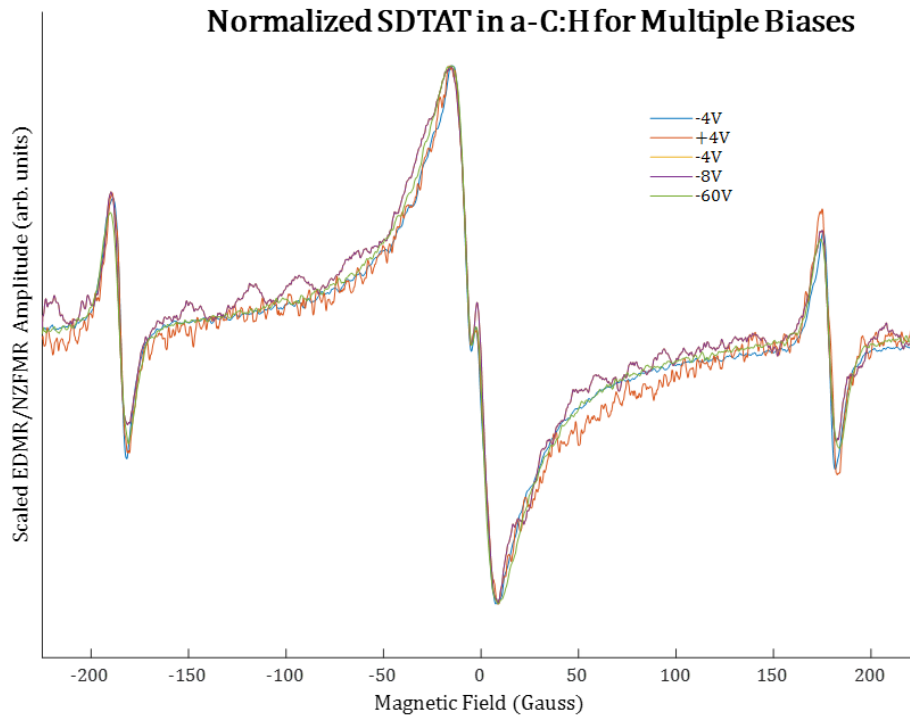


Figure 5.17: Normalized SDTAT spectra for multiple biases during the course of the study. No appreciable change to the shape of either the EDMR or NZFMR spectra can be seen.

We can compare the changes in the measured NZFMR spectra in the a-C:H to the simulated changes from chapter 3.2.4. In this case, only the amplitude of the traces is changing over time and there are no changes to line shape or width. This indicates that only the parameter r_{ea} , the generation rate, is changing during the measurement. This is the rate at which charge carriers enter the material from the environment. This suggests that fewer charge carriers are entering the material which aligns well with the decrease in the measured DC current through the

sample. It would make sense that this reduction in $r_{e\alpha}$ contributes to both the reduction in DC current and the size of the NZFMR response under a constant bias. The likely physical cause of this reduction is trapped charge in the carbon layer increasing the tunneling barrier height. Several samples were annealed at 400K under small positive bias after stressing with no lasting effects on the electronic properties of the samples.

The low field EDMR spectra measured in the a-C:H follow the same trends as the NZFMR spectra. The low field EDMR spectra were narrower than the NZFMR spectra however the line shape and width did not change as the current or bias changed.

The X-band EDMR (9.5 GHz) spectra measured were also broader than the measured low field EDMR (500 MHz) spectra. This broadening is likely due to the disorder in the amorphous system, as no two paramagnetic defects will have identical surroundings. Small strains in the lattice can change the zero-crossing g-value of each individual defect which causes the resonance condition of each defect to be slightly different as well. This range in g-values causes the signal to be spread over a wider range of magnetic field values. This effect is small at low magnetic fields and frequencies; however, it becomes more prominent at higher fields and frequencies. This can be easily understood by looking at the case of only two different g values, 2.002 and 2.003, at two different resonance frequencies, 500 MHz and 9.5 GHz. The resonance condition from chapter 2 is met for the g value of 2.003 at 500 MHz at a magnetic field of 178.35 Gauss. The resonance condition is met for the g value of 2.002 at 500 MHz at a magnetic field of 178.44 Gauss. These two lines would therefore be separated by 0.089 Gauss and would essentially add together to form a single line. The resonance condition is met for the g value of 2.003 at 9.5 GHz at a magnetic field of 3388.7 Gauss. The resonance condition is met for the g value of 2.002 at 9.5 GHz at a magnetic field of 3390.3 Gauss. These two lines would therefore

be separated by 1.7 Gauss. If the lines are broad enough, they may overlap and add to form a single line. This separation is 19 times larger for the 9.5 GHz measurements and would result in a broader line. It is not a coincidence that this factor is exactly the ratio of 9.5 GHz to 500 MHz as the resonance field will increase linearly with resonance frequency. A wider spectrum of g values in an amorphous system would therefore produce a single broad line as all of the different lines for each g -value overlap. The amount that the signal broadens at high resonance fields will correlate to the range of g values in the system, with samples with wider ranges becoming broader as the resonance field and frequency are increased.

Chapter 5.3 EDMR and NZFMR in 1000 nm Thick Amorphous Diamond-like Carbon

SDTAT EDMR and NZFMR as well as other measurements were conducted on 1000nm diamond like (tetrahedral) carbon on p- silicon capacitor dots. The DLC films were deposited using PECVD. The top metal contact is 2mm^2 , composed of approximately 100nm of titanium with approximately $1\mu\text{m}$ of aluminum on top. The composition of the DLC layer is 69% carbon, 27% hydrogen, and 3% nitrogen. The structure of the DLC is shown in Figure 5.18.

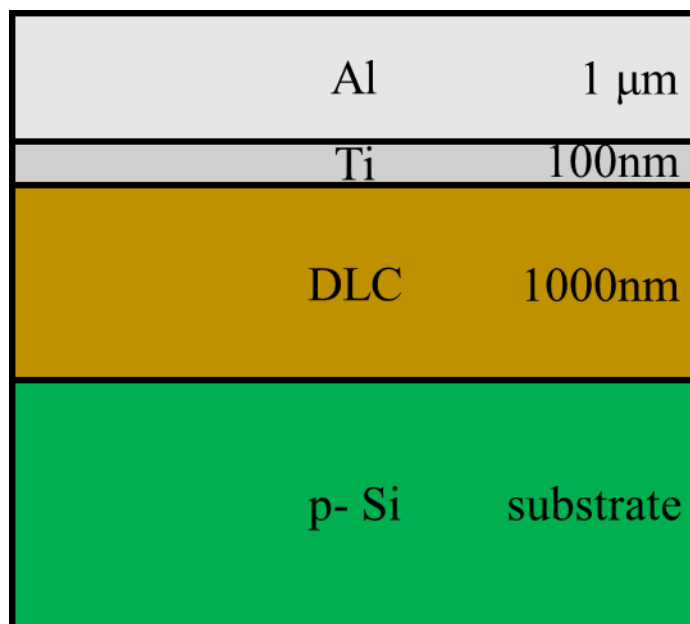


Figure 5.18: Schematic illustration of 1000 nm DLC samples.

Samples were mounted on custom made USB connected PCB “Ts”, with the back contact connected to a bonding pad via electrically conductive paint. Electrical connection to the top contact was made via wire bonding. Under low applied bias, these samples were very stable over long periods of time, however there appear to be changes in the sample at higher applied bias. EDMR and NZFMR signals were only observed when samples were negatively biased.

Chapter 5.3.1 X-band SDTAT EDMR in 1000nm DLC

SDTAT EDMR measurements were made on 1000 nm DLC in order to help identify the defects involved in the electronic transport in the material. The measurements were made on the Bruker X-band spectrometer. A SDTAT EDMR spectrum was measured with the sample biased at -1.5V. This spectrum is shown in Figure 5.19. The magnetic field modulation had an amplitude of 5 Gauss at 12.5 kHz. This modulation frequency is higher than most of the other measurements in this study because this frequency provides the largest signal to noise ratio on

this particular spectrometer. This measured spectrum has a zero-crossing g-value of 2.0041.

The line width of the spectrum was approximately 14 Gauss wide.

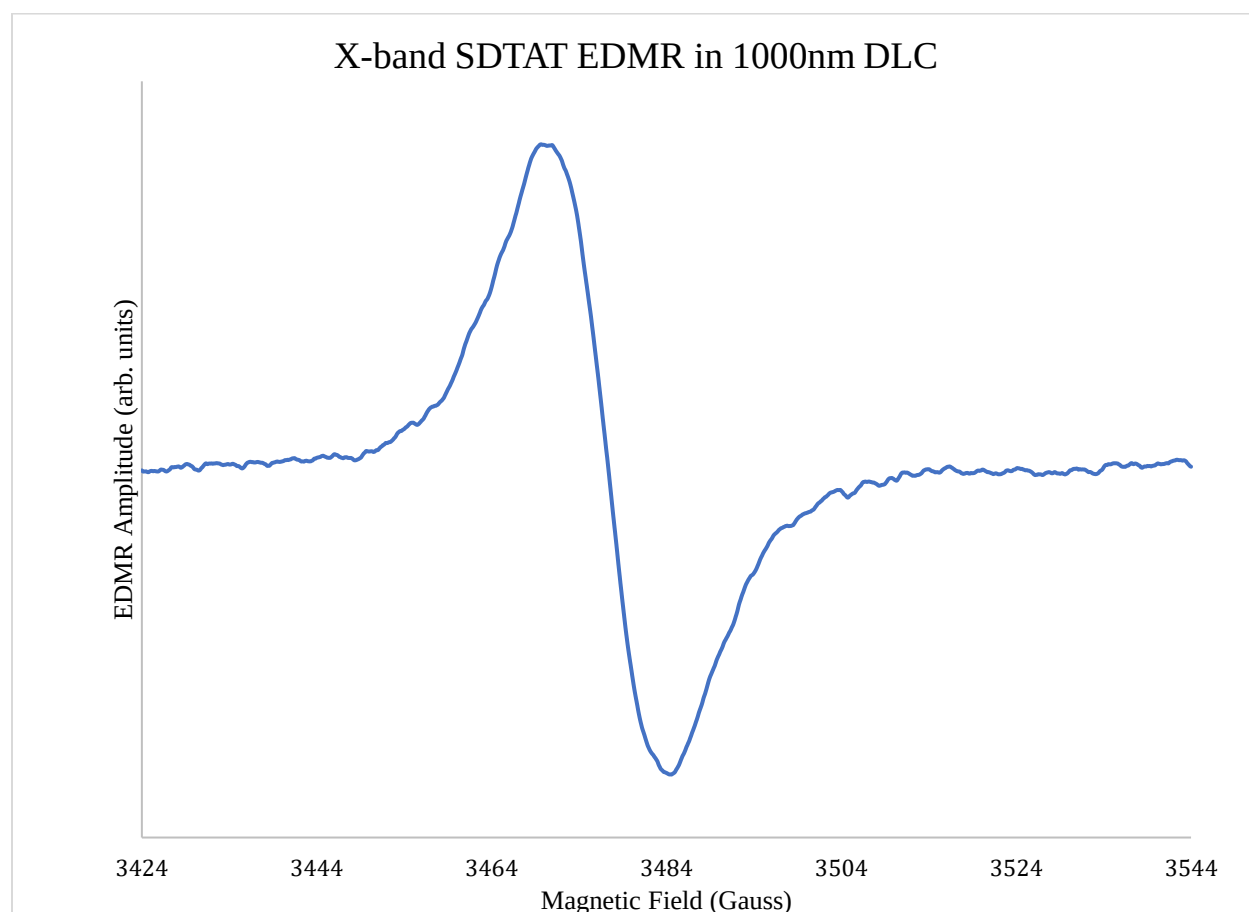


Figure 5.19: X-band SDTAT EDMR spectra in 1000nm DLC. The signal is 14 Gauss wide with a g value of 2.0041.

The defect responsible for the SDTAT EDMR in the 1000nm DLC is likely a dangling bond on sp^2 coordinated sites despite being comprised of half sp^3 coordinated carbons, as discussed in Chapter 5.1. The measured g-value is higher than originally expected but has been seen before in DLC films [83] It could be caused by impurities in the material, [71] however this seems unlikely, as the sample is composed almost entirely of carbon and hydrogen, with only 2% nitrogen.

Chapter 5.3.2 SDTAT NZFMR and Low Field EDMR in 1000nm DLC

After performing X-band SDTAT EDMR on these samples, SDTAT NZFMR and low-field EDMR were performed on fresh samples. These measurements were made on both the Kepco LF/ZF spectrometer and the Blue Spin LF/ZF spectrometer. The Kepco LF/ZF spectrometer was primarily used when the DC current in the samples had to be measured during the low-field EDMR/NZFMR measurements.

SDTAT NZFMR measurements on the DLC at multiple applied biases is illustrated in Figure 5.20. The NZFMR amplitude increases with bias until approximately -1.5V. Higher magnitude bias (more negative) causes the NZFMR signal to become slightly smaller, then hold relatively constant at biases greater than -3V. The wider signal appears to maintain its shape and line width however the center inflection appears to change shape and increases in amplitude with increasing bias. Under a large constant bias, the inflection continues to change over time. The low bias measurements were made on the Blue-Spin LF/ZF spectrometer.

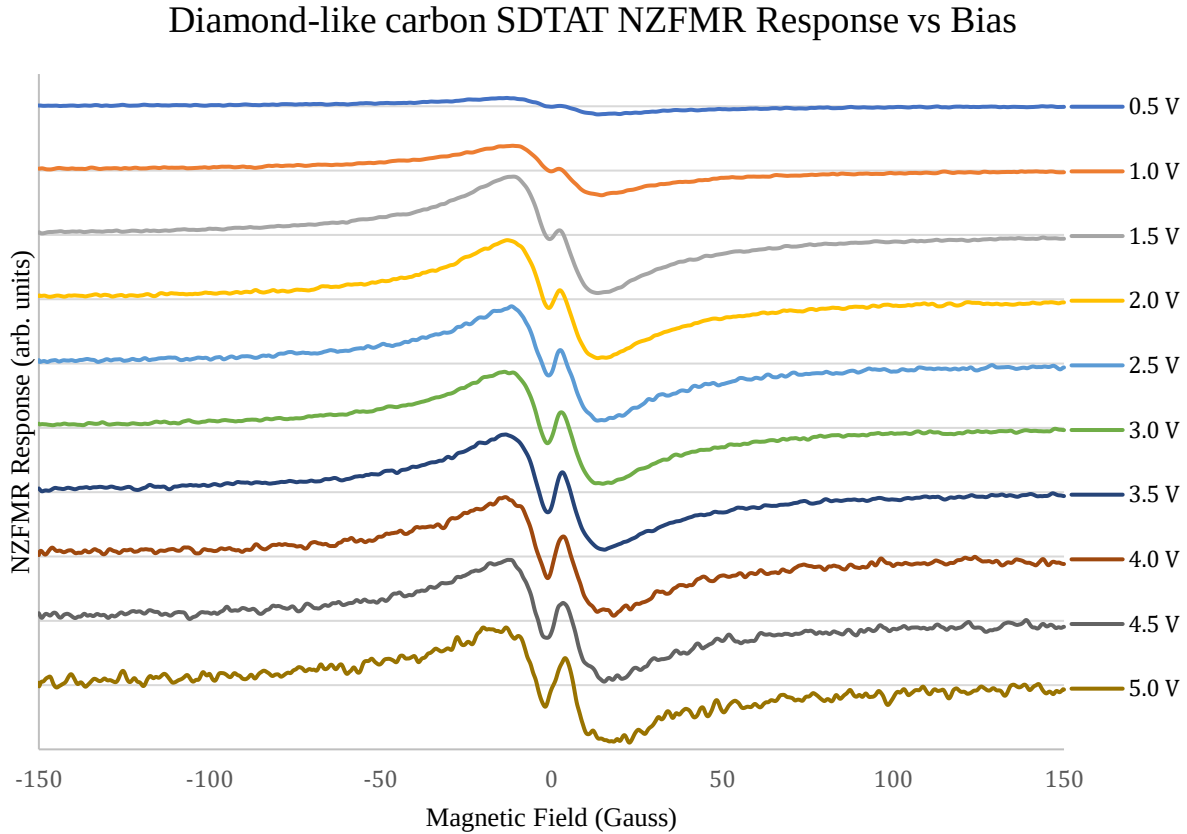


Figure 5.20: SDTAT NZFMR response vs bias in 1000nm diamond-like carbon. Amplitude of signals is not normalized. Measurements made using 3 Gauss modulation amplitude.

Figure 5.20 shows that, unlike in the a-C:H samples, the shape of the line changes with bias. In this case with low applied biases, there are different variables changing from Figure 3.4. Here the amplitude of the spectra increases as the bias is increased from -0.5V to -1.5V, indicating that $r_{e\alpha}$ changes. The change in the amplitude of the inflection also indicates that more than one variable is changing. The changes seen in these measured spectra are similar to the changes seen in the simulated spectra for a decrease in $r_{\alpha e}$ from Figure 3.4.

Spectra were simulated and fit utilizing the least squares fitting outlined by Frantz et al. [64] for the cases of -1V, -2V, and -3V applied to the samples. These cases were chosen because

of the high signal to noise ratio of the measured spectra, and the stability of the samples during the measurements. There were no large changes in the DC current or measured spectra at the low biases. The fitting algorithm was again constructed to only consider the hyperfine contributions of a single species which was assumed to be hydrogen, the most abundant magnetic nucleus in the sample.

The simulated spectra are shown in Figure 5.21. The resulting hyperfine coupling constants for sites α and β were both found to be 3.8 ± 0.5 Gauss. This value was constant for all three simulations as the defect responsible for conduction does not appear to be changing, with all measured spectra being repeatable at low biasing conditions. For this reason, the singlet probability of hopping rate was also constant for all three simulations. The fitting produced a hopping rate, $r_{\alpha\beta}$, of 490 ± 50 MHz, while the generation rate, $r_{e\alpha}$, and dissociation rate, $r_{\alpha e}$, were allowed to vary for the different cases. The fitting for the case of -1V applied to the sample produced values for a generation rate, $r_{e\alpha}$, of 3.8 ± 0.25 GHz and a dissociation rate, $r_{\alpha e}$, of 110 ± 10 MHz. The fitting for the case of -2V applied to the sample produced values for a generation rate, $r_{e\alpha}$, of 6.4 ± 0.25 GHz and a dissociation rate, $r_{\alpha e}$, of 100 ± 10 MHz. The fitting for the case of -3V applied to the sample produced values for a generation rate, $r_{e\alpha}$, of 4.3 ± 0.25 GHz and a dissociation rate, $r_{\alpha e}$, of 90 ± 10 MHz.

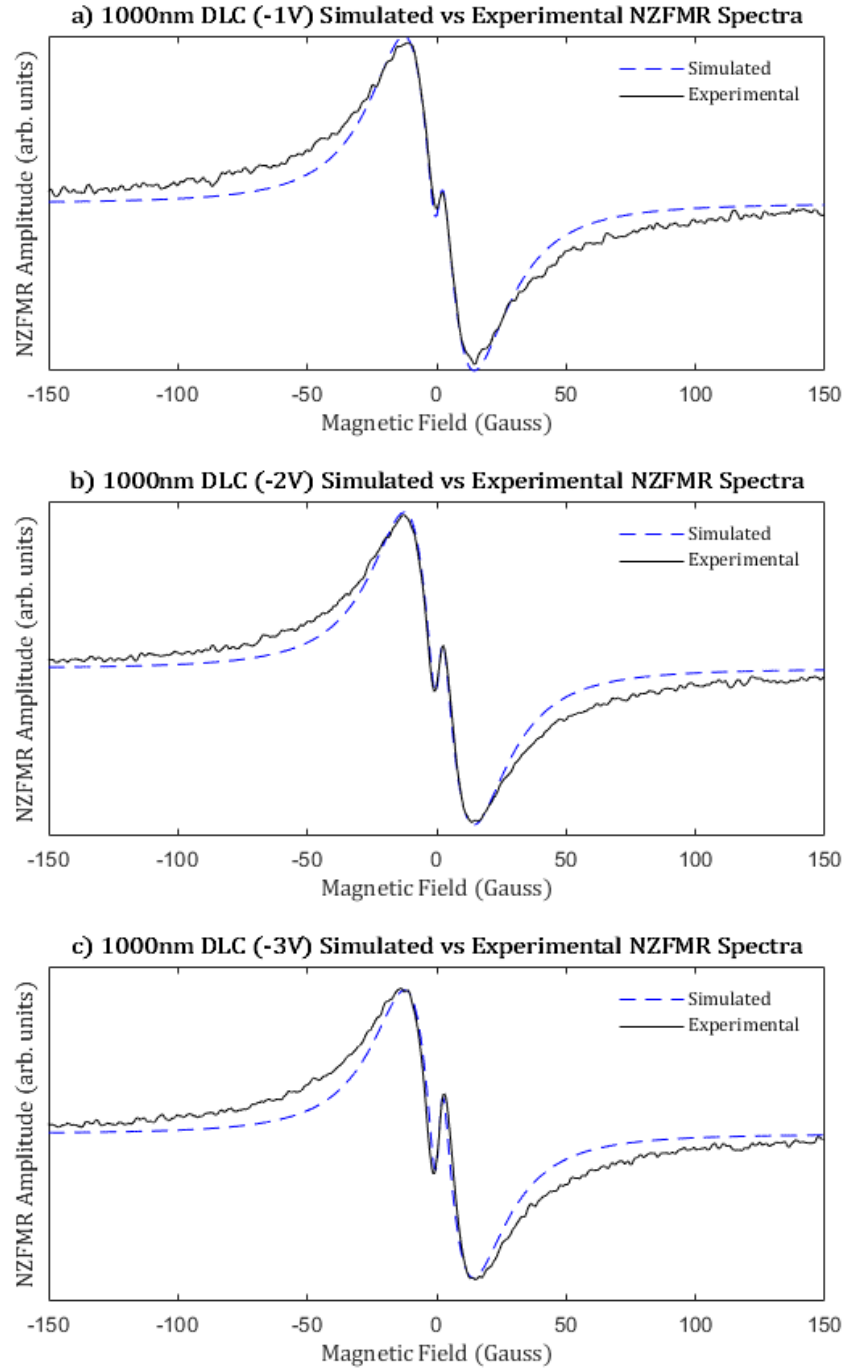


Figure 5.21: Simulated and measured NZFMR spectra in DLC for multiple biasing conditions. a) -1V applied to sample, simulation parameters $r_{e\alpha} = 3.8 \pm 0.25 \text{ GHz}$, $r_{\alpha e} = 110 \pm 10 \text{ MHz}$, $r_{\alpha\beta} = 490 \pm 50 \text{ MHz}$, and hyperfine coupling constants on both sites of $3.8 \pm 0.5 \text{ Gauss}$. b) -2V applied to sample, simulation parameters $r_{e\alpha} = 6.4 \pm 0.25 \text{ GHz}$, $r_{\alpha e} = 100 \pm 10 \text{ MHz}$, $r_{\alpha\beta} = 490 \pm 50 \text{ MHz}$, and hyperfine coupling constants on both sites of $3.8 \pm 0.5 \text{ Gauss}$. c) -3V applied to sample, simulation parameters $r_{e\alpha} = 4.3 \pm 0.25 \text{ GHz}$, $r_{\alpha e} = 90 \pm 10 \text{ MHz}$, $r_{\alpha\beta} = 490 \pm 50 \text{ MHz}$, and hyperfine coupling constants on both sites of $3.8 \pm 0.5 \text{ Gauss}$.

The fittings from these simulations indicate that the dissociation rate, r_{ae} , is the primary variable that changes in the DLC as the bias is changed. The generation rate, r_{ea} , changes as well, but is mostly used as a scaling factor in the simulations. The dissociation rate decreases in this sample as the bias is increased, from a value of 113 MHz at -1V to 87MHz at -3V, causing the center inflection line to become larger.

These values appear to be plausible as the hyperfine coupling constant is a value between the approximately 1 Gauss lower limit and the 9 Gauss low-field EDMR line width. A hopping rate larger than the dissociation rate is also plausible as the current is dominated by hopping events and larger biases lead to increased hopping rates relative to dissociation rates. The hyperfine coupling constant is larger for the DLC than for the a-C:H even though it has a slightly lower hydrogen content. This may be due to the higher coordination of the carbon atoms in the DLC as about half of them are sp^3 coordinated unlike the a-C:H in which all of the carbon atoms are sp^2 coordinated. This would provide a higher probability of one or more hydrogen atoms being near the sp^3 coordinated carbon. This higher hyperfine coupling constant is also consistent with the broader low-field EDMR line width of 9 Gauss in the DLC compared to 7 Gauss in the a-C:H. The low-field EDMR linewidth is dominated by hyperfine interactions so a larger hyperfine coupling constant would cause the low-field linewidth to be larger.

One might expect a larger dissociation rate at higher bias as the tunneling barrier shifts from trapezoidal towards a triangular shape and transport shifts from spin dependent site to site hopping to more of a spin-independent direct tunneling, however, this does not appear to be the case. This may be due the thickness of the samples, approximately 1 micron thick, resulting in very few direct tunneling events at the biasing conditions used in this study. Further studies at higher bias may provide some insight into this somewhat unexpected behavior.

The DC current does not change in the DLC samples at low applied biases and these signals did not change over time, however, the change in center inflection over time at higher bias (greater than -5V) suggested that it would be useful to increase the bias further and monitor both the DC current in the sample and the changes to the SDTAT NZFMR signal over time. This meant using the Kepco LF/ZF spectrometer to perform NZFMR on the DLC under a larger bias of -7.5V. There were significant changes to both the DC current and the measured spectra over time. Unlike the 500nm a-C:H, the DC current in the DLC increased over time and the spectrum changed shape, with the narrow center inflection becoming larger in amplitude than the wider signal. This change is shown in Figure 5.22. The signal to noise ratio is severely reduced at higher biases and currents in these samples. This measurement was made in conjunction with other students in the laboratory group, namely Elias Frantz and Ryan Waskiewicz.

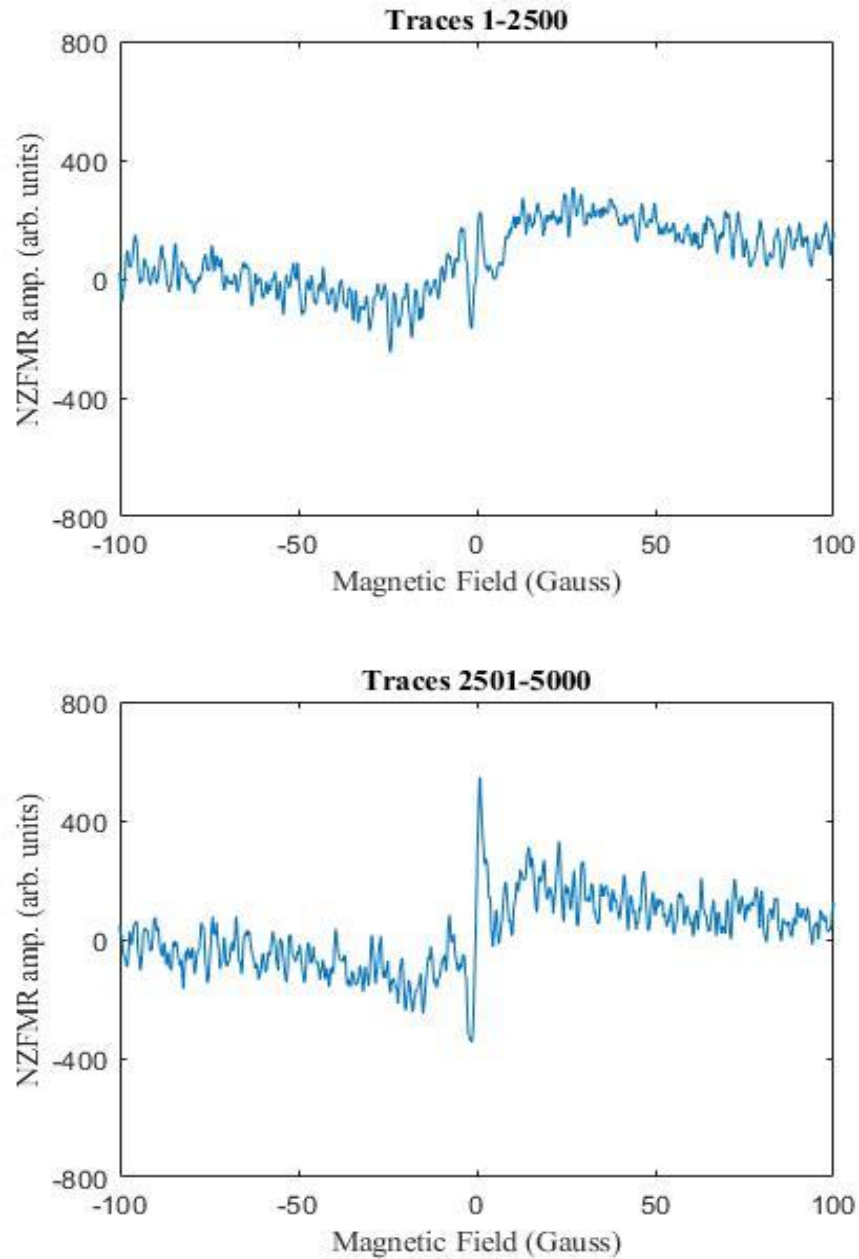


Figure 5.22: Top) Averaged SDTAT NZFMR spectrum of 1000nm DLC biased at -7.5V (first 2500 traces)
 Bottom) Averaged SDTAT NZFMR spectrum of 1000nm DLC biased at -7.5V (last 2500 traces)
 Note the change in the size of the center inflection over time while the wider signal remains mostly unchanged.
 Both plots use the same scale for the vertical axis.

The current in the sample was monitored during the SDTAT NZFMR measurement and is shown in Figure 5.23. The current increases over time corresponding to the increase in the size of the center inflection signal.

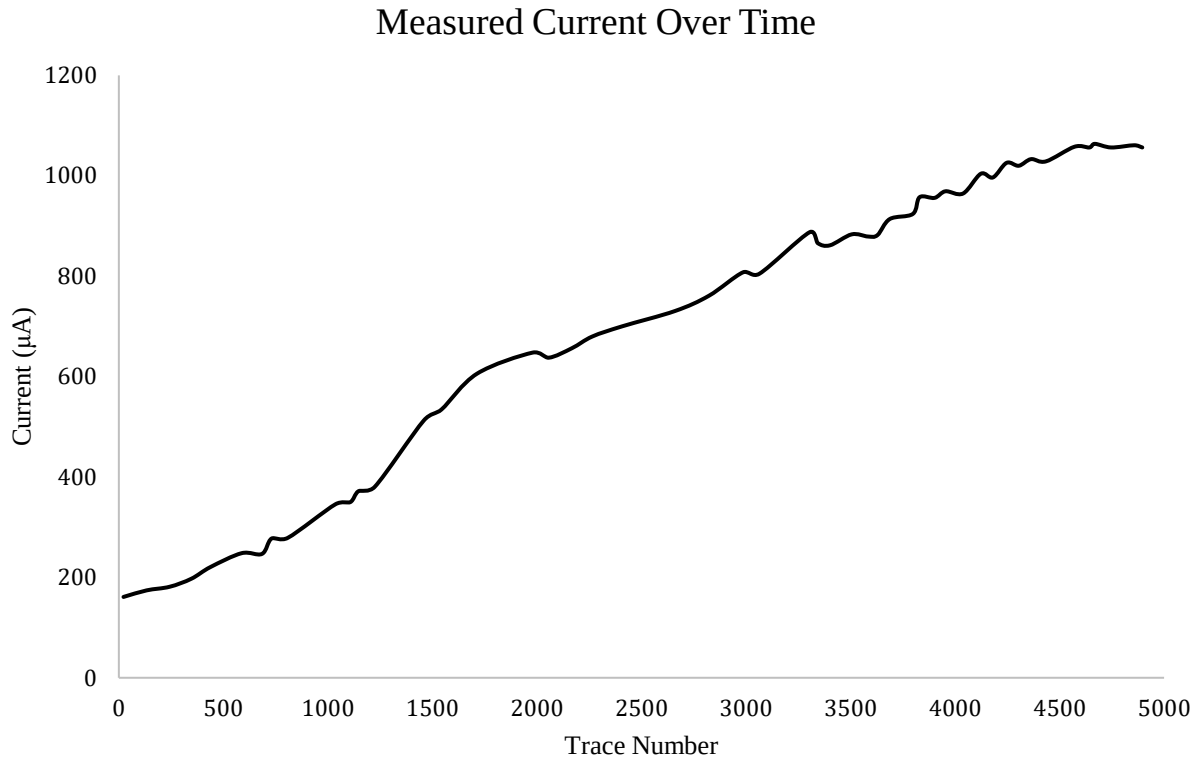


Figure 5.23: DC current in 1000nm DLC under constant -7.5V bias during SDTAT NZFMR.

The change in line shape over time, and not just signal amplitude, suggests that an additional defect forms and is likely also responsible for the spin dependent conduction through the material. The low signal to noise of the spectra measured at higher biasing conditions prevents accurate simulations from being calculated, although the introduction of a new defect in the system could be a symptom of stress induced leakage current or a time dependent dielectric breakdown-like process, if not both.

The low field SDTAT EDMR response at low bias in the 1000nm DLC follows a pattern similar to the NZFMR response at low bias, with the signal amplitude increasing until the applied bias is approximately -1.5V. After -1.5V the signal decreases slightly but stays fairly constant at higher magnitude bias. This can be seen in Figure 5.24 in which the spectra are not normalized. The EDMR response signal to noise ratio also suffers at higher bias and increased DC current. These measurements were made on the Blue-Spin LF-EDMR/NZFMR spectrometer.

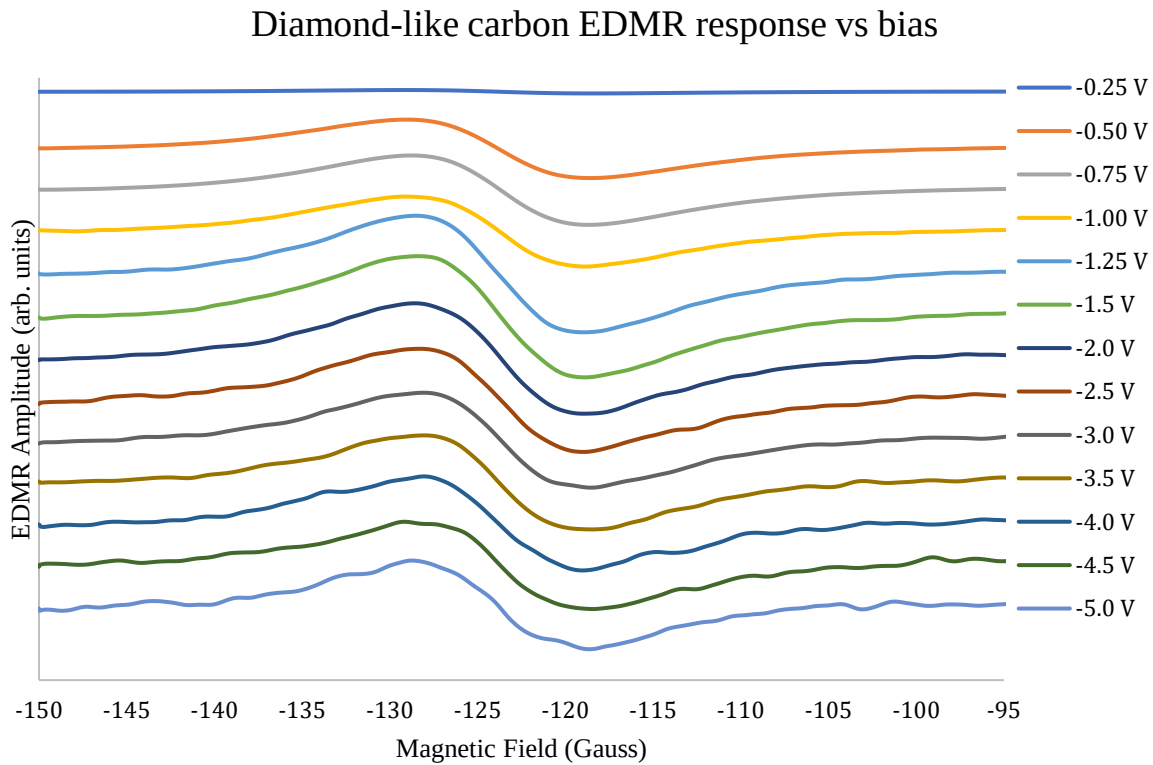


Figure 5.24: SDTAT EDMR response vs bias in 1 μm diamond-like carbon. Amplitude of signals is not normalized. Measurements were made using a 5 Gauss modulation amplitude.

The change in the low-field EDMR signal at low bias, with the amplitude reaching a maximum around -1.5V then staying roughly constant, matches the NZFMR measurements,

suggesting that the defects responsible for conduction in these cases are likely the same. Low field EDMR is difficult to perform at higher biases due to the reduced SNR, however, these measurements will likely be part of any future work on these samples. The line-width of this sample also changes from 9 Gauss wide at 370 MHz to 14 Gauss wide at 9.5 GHz, suggesting a wider range of g values in the DLC than in the a-C:H, as described earlier.

Chapter 5.4 Discussions about a-C, Contributions to Theory, and Future Work

The changes in the amorphous carbon samples over time under constant bias provide an opportunity to improve our models of both EDMR and NZFMR and also, to some extent, develop an understanding of SILC and TDDB in these model systems. The changes observed in the 500nm a-C:H, the diminishing DC current and SDTAT signals over time, might be linked to a TDDB process in which hopping sites close to the edge of the material are occupied by charge carriers. Occupation by a charge carrier may increase the barrier that another charge carrier must overcome in order to tunnel through the material as seen in Figure 5.15. The larger barrier makes it more difficult for a charge carrier to tunnel to another site which could potentially explain the reduction in current and the drop in signal amplitude if the critical hopping distance is getting longer as sites are blocked due to being filled and the tunneling probability is decreased due to the potential well getting deeper as the barrier height increases.

The general shape of the spectra measured in the a-C:H remains the same across a wide range of biases and charge states and only the amplitude of the signal appears to change as measurements are performed on the samples. Comparing the changes in the SDTAT NZFMR response in the a-C:H to the simulations in Chapter 3.2.4 indicates that the only parameter that is changing in these samples is the generation rate at which carriers are entering the initial site from

the environment. That is, only r_{ea} is changing while the other variables from equations 3.2.5 and 3.2.6, r_{ab} , r_{ae} , a_α , and a_β , are remaining constant. This would indicate that the trapped charges are likely localized to a thin region near the interface as the density of defects through which the carrier's travel does not appear to change because the hopping rate, r_{ab} , remains constant.

The changes seen in the 1000nm DLC provide evidence that the center inflection signal likely arises from a different pathway than the broader, usually larger signal. Some attempts have been made by collaborators to model this change using the adapted two site model for SDTAT in inorganic materials. The most promising attempt, though not fully developed and discussed in a private communication, appears to use two separate spin mixing pathways in order to achieve the measured spectra, with the relative contributions of each to the total spectrum changing over time. [87]

The variables from equations 3.2.5 and 3.2.6 that appear to be changing in the DLC samples are r_{ae} , and r_{ea} , as variations in the first value affects the size of the inflection response relative to the size of broader signal, while the increased current is likely due to an increase in the initial generation rate. It appears that there may be a reduced dissociation rate, r_{ae} , the rate at which carriers hop from a trapping site is not spin dependent when hopping to an environment with more possible states to occupy. These changes would indicate that the path the carrier is taking through the material is changing as the voltage, current, and time stressed are increased.

The simulated spectra fitted in this section agree well with the peaks of the measured spectra at lower magnetic field. There is, however, some discrepancies between the tails of the measured and simulated spectra. This could be caused by another interaction that is not accounted for in the models. The model only accounts for the effects of a single species,

assumed to be nearby hydrogen nuclei as they are the most abundant magnetic species in the samples. Further development of the computational model may be able to account for more interactions.

Both material systems have broader EDMR linewidths at X-band (9.5 GHz) than at low-field (370 MHz). The spectra measured in the DLC samples appear to broaden more than the spectra measured in the a-C:H. The EDMR linewidth of the a-C:H changes from 7.5 Gauss at 500 MHz to 9 Gauss at 9.5 GHz, a difference of 1.5 Gauss. The EDMR linewidth of the DLC changes from 9 Gauss at 370 MHz to 14 Gauss at 9.5 GHz, a difference of 5 Gauss. This would suggest that there is wider range in g values in the DLC. This result seems to make sense as most of the electron orbitals around the carbon atoms in the a-C:H are sp^2 hybridized while the electron orbitals around carbon atoms in the DLC are a mix of sp^2 and sp^3 hybridized, leading to more disorder and a wider range of g values for the individual defects that contribute to the spectrum. The broader low-field linewidth in the DLC suggests that the hyperfine interactions are stronger in these samples, which is consistent with the larger extracted hyperfine coupling constant from the simulated spectra.

Future work on these samples will likely involve finding ways to safely stress the 500nm a-C:H until hard breakdown occurs to observe the change in the EDMR and NZFMR signals as the material approaches failure. The signal to noise ratio of the 1000nm DLC samples will also have to be increased at the higher, -7.5V, bias to be able to fit the data with simulated spectra. This can likely be achieved by increasing the amount of time the samples are signal averaged for while monitoring the changes in the DC sample current and NZFMR spectrum over time. The changes in the DLC samples at higher bias might then be described quantitatively by fitted simulated spectra.

Chapter 6

Electrically Detected Magnetic Resonance and Near Zero Field Magneto-Resistance in Amorphous Silicon Carbide

SDTAT EDMR and NZFMR measurements were made on 5nm amorphous hydrogenated silicon carbide (a-SiC:H) on p⁺⁺ silicon MOS capacitors. These thin film samples contain approximately 32% hydrogen. The a-SiC:H was deposited via PECVD. The top metal contact is 2mm², composed of approximately 100nm of titanium with approximately 1μm of aluminum on top. The structure of the a-SiC:H is shown in Figure 6.1.

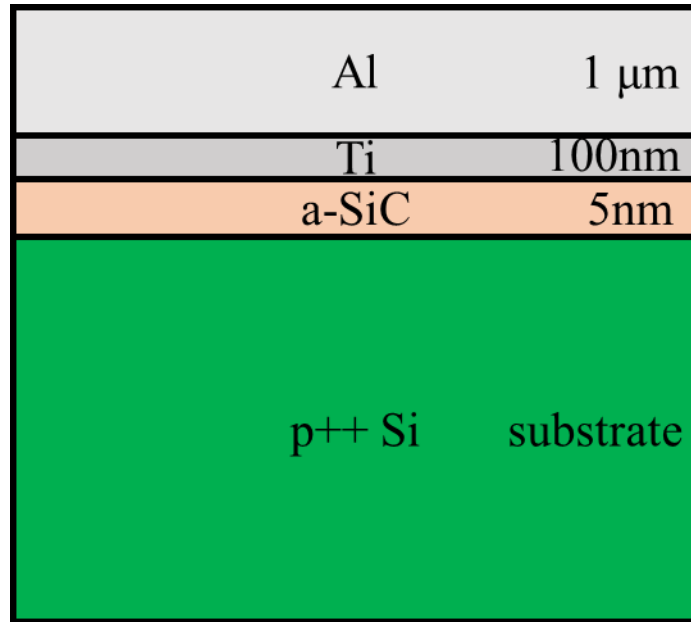


Figure 6.1: Schematic illustration of 5nm a-SiC:H samples.

These a-SiC:H samples showed no instabilities over a wide range of biases. The very high signal to noise ratio of these samples could be potentially useful in the development of spin-based magnetometers like the one proposed by Cochrane et al. [43] as materials with large signals and narrow line widths allow for a higher sensitivity in this type of magnetometer.

Most samples were mounted on custom made USB connected PCB “Ts”, with the back contact connected to a bonding pad via electrically conductive paint. Electrical connection to the top contact was made via wire bonding. These samples were characterized using the HP model 4155 semiconductor parameter analyzer and Boonton model 72B capacitance meter; however, no changes were seen over time.

Some samples were not attached to any external mount for NZFMR measurements. These samples were placed onto a wafer probing station in a small home-built wire wound electromagnet with enclosed modulation coils. Electrical contact to the back of these samples was made by placing the sample on a sheet of copper foil which was electrically isolated from the chuck of the probing station. The probes used to make contact to the sample were placed on the top contact of the MOS capacitor and the copper foil the sample was resting on. It should be noted that unlike the other samples in this work which have to be bonded to the PCB “T” and connected via wire bonds, no sample preparation was required in order to make NZFMR measurements on these samples. This is discussed further in appendix B.

Chapter 6.1 X-Band SDTAT EDMR in 5nm a-SiC:H

SDTAT EDMR measurements were made on 5nm a-SiC:H using the home-built Lakeshore X-band spectrometer. The lock-in detection for these measurements utilized a field modulation amplitude of 5 Gauss at approximately 1000 Hz. An X-band SDTAT EDMR spectrum for the a-SiC:H is shown in Figure 6.2. This measurement was made with the sample top contact biased at +2V and a modulation frequency of 1150 Hz.

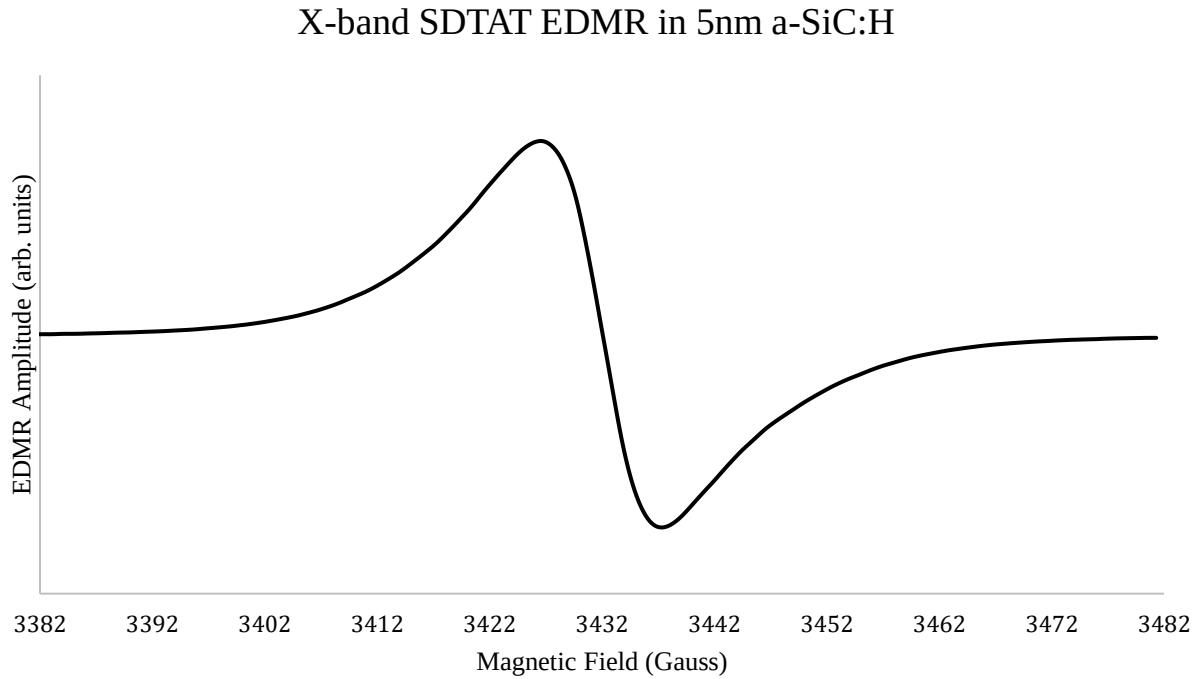


Figure 6.2: X-band SDTAT EDMR in 5nm a-SiC:H. Sample biased at +2V. The signal is 10.8 Gauss wide. This defect has a zero-crossing g value of 2.0032.

The measured spectrum has a linewidth of 10.8 Gauss and a zero-crossing g value of 2.0032. A series of measurements at different biases was made yielding spectra of different amplitudes but with similar line shapes. The line shapes of the normalized measured spectra are compared in Figure 6.3.

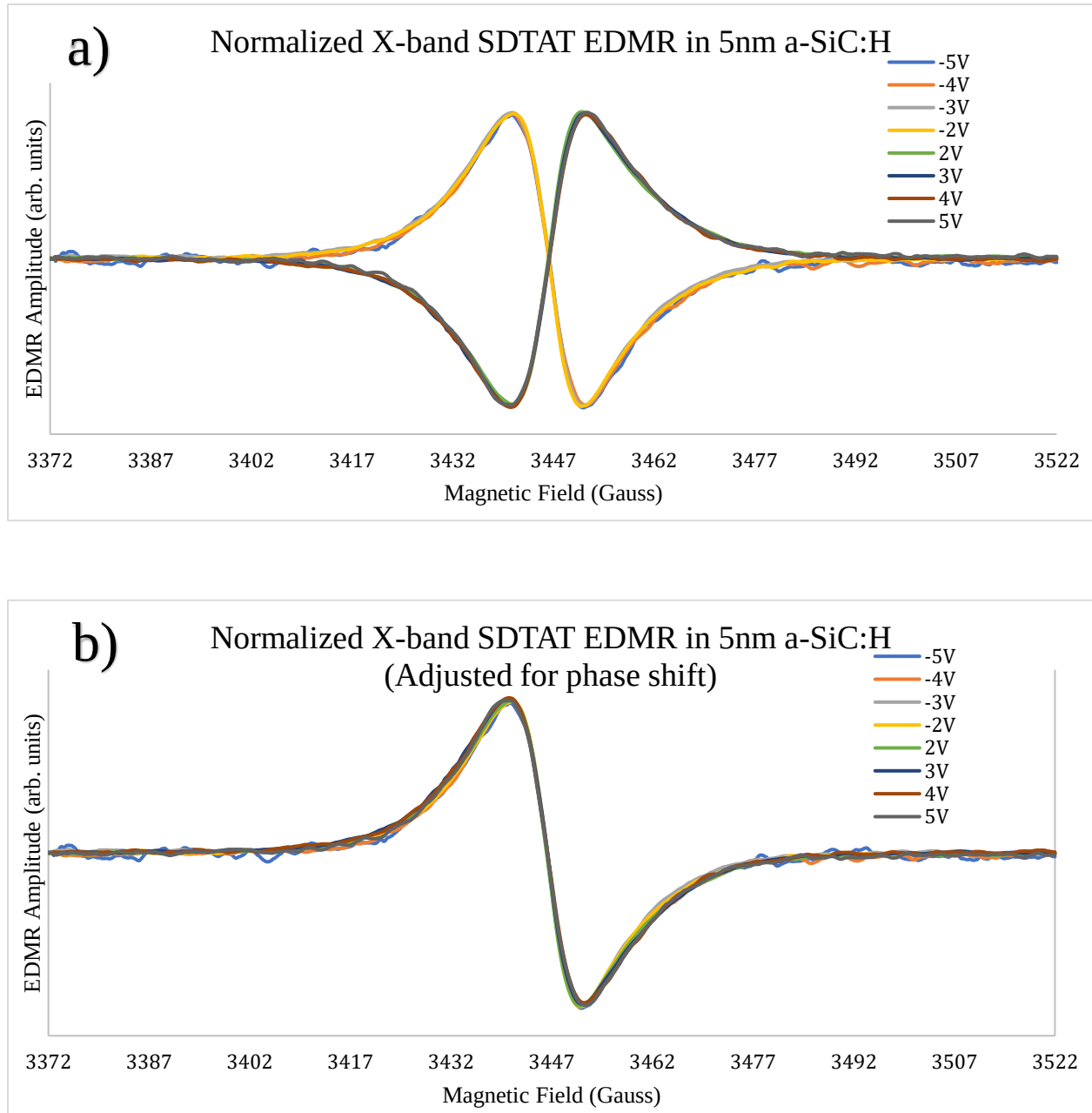


Figure 6.3: Normalized SDTAT EDMR spectra in 5nm a-SiC:H. a) Spectra showing phase of signal changes due to inverting polarity of the applied bias. b) All spectra with same phase.

There is no change in the linewidth or general line shape of the signals with the same polarity of applied bias. Inverting the normalized signals measured under a positive applied bias shows that the line shape of all signals is essentially identical across all measured applied biases.

The only difference between the X-band SDTAT EDMR spectra at different biases is the amplitude of the response. The amplitude of the EDMR response at different biases is shown in Figure 6.4, showing an exponential growth in the signal amplitude with bias, although the signal amplitude is larger at positive applied bias.

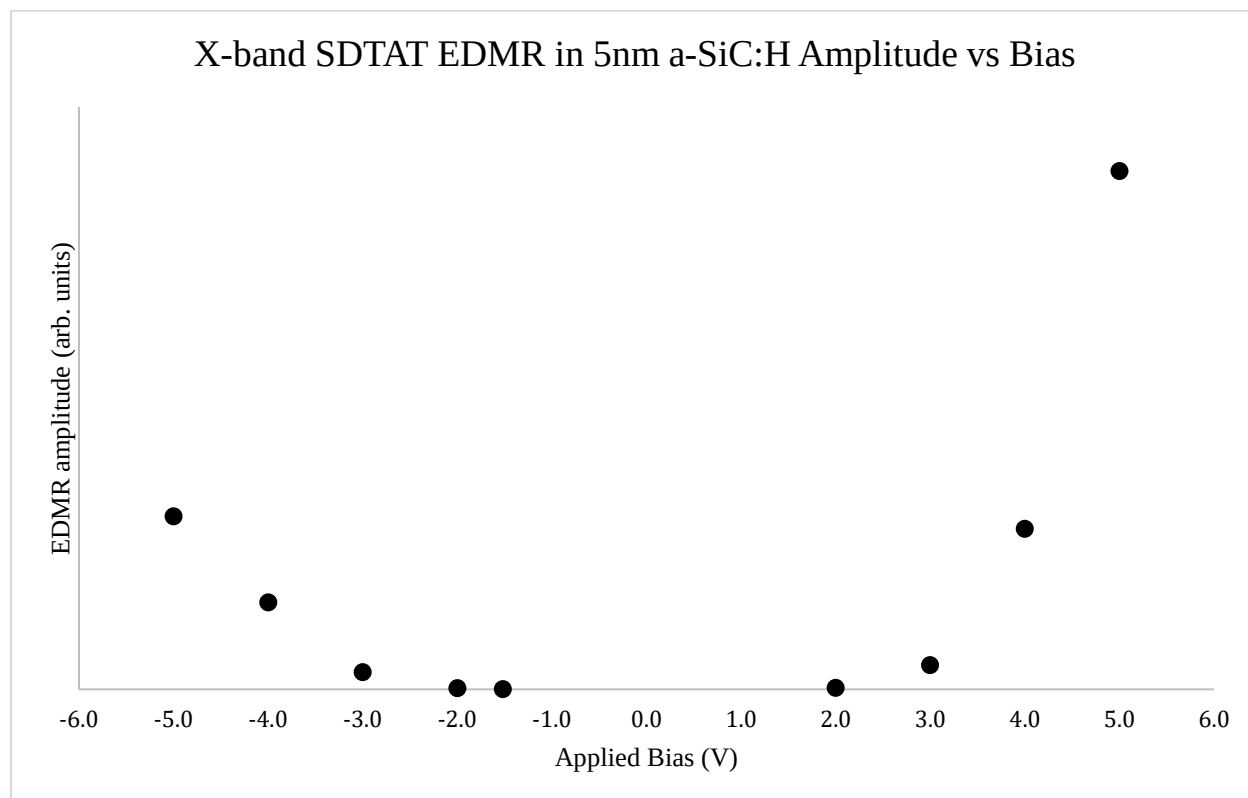


Figure 6.4: X-band SDTAT EDMR amplitude vs bias in a-SiC:H. Larger signals are measured at positive bias.

Chapter 6.2 NZFMR and Low Field EDMR in 5nm a-SiC:H

Due to the stability of the 5nm a-SiC:H, the same samples studied at X-band were studied using NZFMR and low field EDMR. These measurements were made on the Blue-Spin LF/ZF spectrometer. EDMR and NZFMR measurements were made at biases between -5V and 5V. Normalized spectra at several applied biases are shown in Figure 6.5. Unlike the X-band and low-field SDTAT EDMR response, the NZFMR linewidth changes with applied bias, becoming

slightly wider with increasing bias magnitude (both positive and negative). The relative size of the EDMR to the NZFMR response also changes with bias, initially increasing with increased bias, reaching the maximum relative size of the EDMR at an applied bias of +3V, then becoming smaller with increasing bias. This is a curious effect and likely arises from the different mechanisms that give rise to each signal in this material, with EDMR being caused by spin flipping, and NZFMR caused by spin mixing.

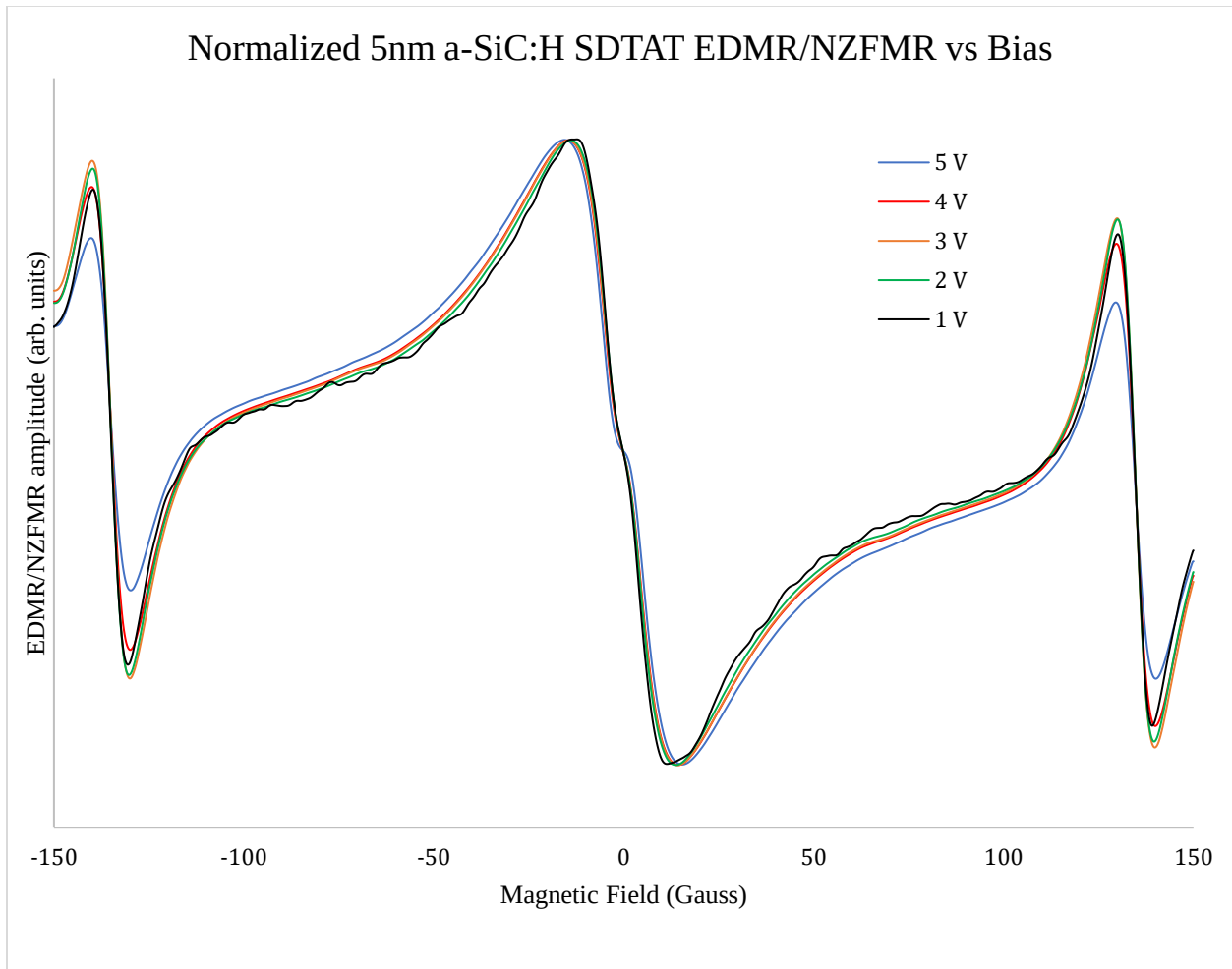


Figure 6.5: Normalized SDTAT EDMR/NZFMR response in 5nm a-SiC:H. Relative to the NZFMR response, the amplitude of the 8 Gauss wide EDMR signal proportionally increases until it reaches 3 V, then decreases as the bias is increased. The NZFMR response becomes wider with increased bias from 25 Gauss at 1V to 31 Gauss at 5V. Measurements were made using a 5 Gauss modulation amplitude.

The magnitude of the SDTAT NZFMR response, shown in Figure 6.6, follows a similar pattern to the X-band SDTAT EDMR, increasing at higher bias and larger for positive applied bias than for negative.

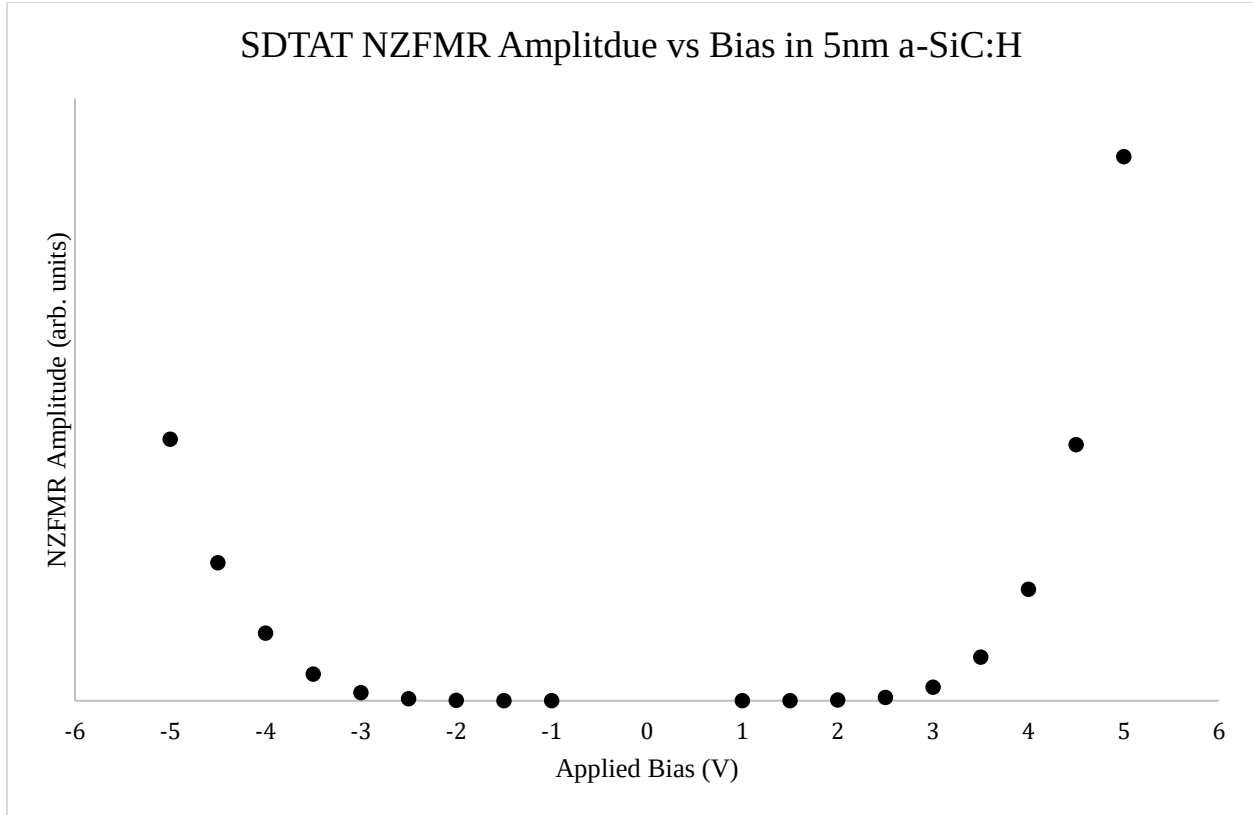


Figure 6.6: SDTAT NZFMR amplitude vs bias in 5nm a-SiC:H.

The defect responsible for conduction could either be related to silicon or carbon atoms as both are present in the material. One method to determine which species is likely involved is discussed by Mutch. [88] An approximate range of g values, Δg , can be calculated for a sample by using the difference in the linewidths of spectra measured at very different resonance frequencies. The linewidth measured at X-band was 10.8 Gauss while the low-field EDMR signal was 8 Gauss wide; a difference of 2.8 Gauss. This corresponds to a $\Delta g = 0.0016$. The

Δg value for a silicon dangling bond in a-Si:H is approximately 0.0044 while the Δg value for a carbon dangling bond in a-C:H is approximately 0.0011. [88] The Δg value for the defect in the a-SiC:H in this study is very close to the Δg value for carbon dangling bonds in a-C:H and therefore these spectra are attributed to carbon dangling bonds.

SDTAT NZFMR measurements without the RF oscillating B_1 were made over a series of applied biases using a smaller magnetic field modulation amplitude of 1 Gauss to resolve the center inflection signal. These measurements are shown in Figure 6.7. The NZFMR measurements made without the RF B_1 oscillating magnetic field appear to be essentially identical to the NZFMR response when the oscillating B_1 field is present and the line width of the NZFMR response increases with larger magnitude applied bias.

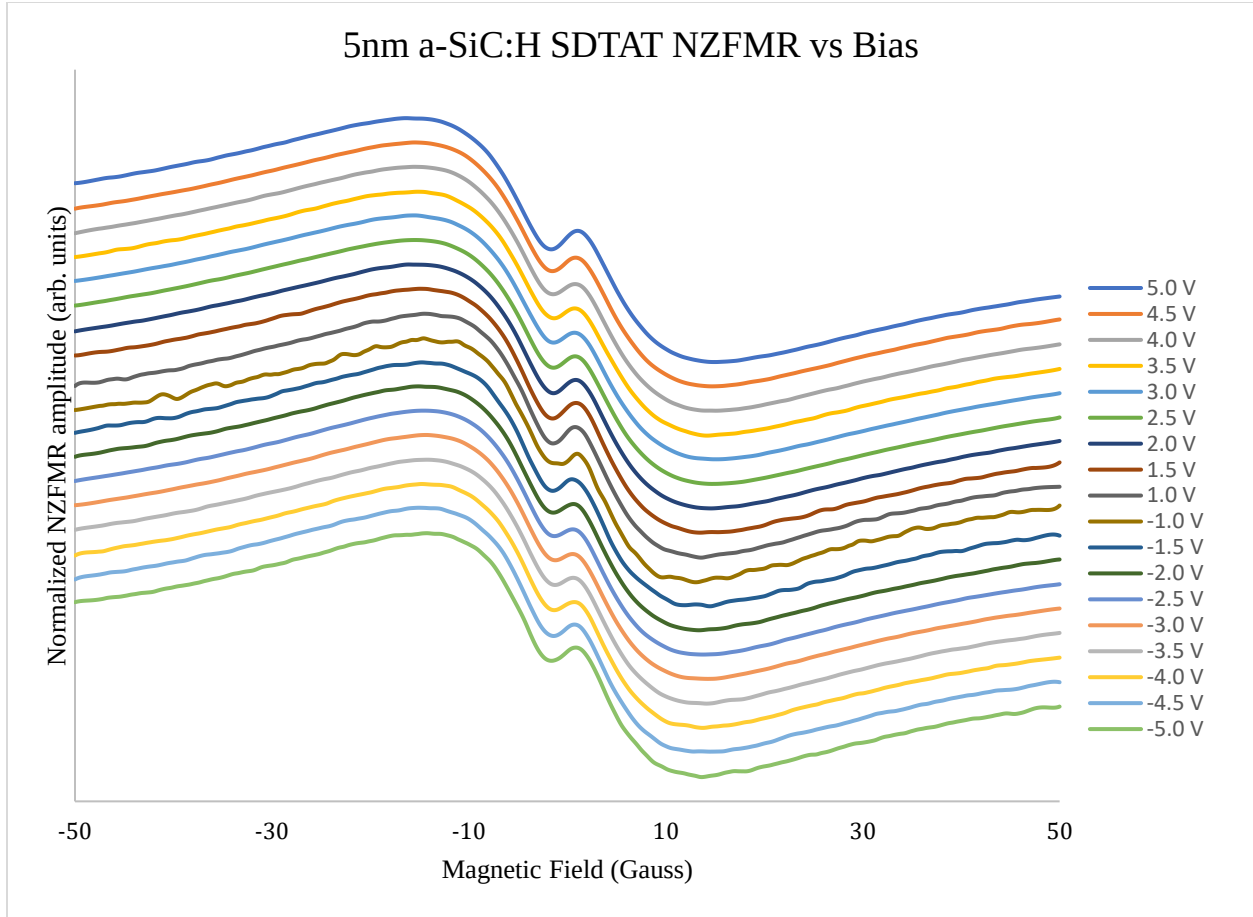


Figure 6.7: Normalized SDTAT NZFMR in a-SiC:H for multiple applied biases without oscillating B_1 magnetic field. The NZFMR response becomes wider with increased bias from 25 Gauss at 1V to 31 Gauss at 5V. The inflection linewidth stays at a roughly constant value of 2.3 Gauss.

This response suggests that the parameters from Figure 3.4 that are changing include $r_{e\alpha}$ due to the increased signal amplitude, and $r_{\alpha\beta}$ and $r_{\alpha e}$ which can both affect the width of the NZFMR response. The spin system for a-SiC:H is probably too complicated [89]–[91] for the current models to simulate, and as such, no simulations have been made regarding the a-SiC:H. Qualitative comparisons to the plots from chapter 3.4.2, however, strongly suggest that the dissociation rate, $r_{\alpha e}$, is decreasing and the hopping rate, $r_{\alpha\beta}$, is increasing as both of these changes to these parameters would cause the broad line to become wider. Each change would

affect the amplitude of the inflection line in an opposite way so a combination of these two changes could keep the center inflection line constant, essentially canceling each other out. Future work on this material system will likely involve improving modeling capabilities to account for the more complex nature of the SiC spin system.

Chapter 6.3 Lock-in Phase Dependent Responses

The large signal to noise ratio of the a-SiC:H samples allows for a curious phenomenon to be seen in which the spectrum line shape is different depending on the phase detection angle of the lock-in amplifier. This is most easily seen during an EDMR and NZFMR measurement where the phase of the EDMR response can be flipped with respect to the phase of the NZFMR response by careful selection of a lock-in detection phase. This is shown in Figure 6.8 where the two spectra have the same phase orientation for the NZFMR response (down-up-down) but have opposite phase orientation for the EDMR response (up-down-up vs down-up-down). These two spectra were measured simultaneously under identical experimental conditions, with the only difference between them being the detection phase used by the lock-in amplifier. These signals are interpreted by the lock-in amplifier 90 degrees apart. It should be noted that the top spectrum is much smaller than the bottom spectrum. There is also a discrepancy between the size of the center inflection of the NZFMR signals, with the relative size of the inflection in the top signal being significantly larger than that of the bottom. This measurement was made using the Blue Spin LF/ZF spectrometer. The change in the relative amplitude of the center inflection suggests that the center inflection and broad signal arise from different physical mechanisms which newer models will have to account for in order to extract information about what those mechanisms may be.

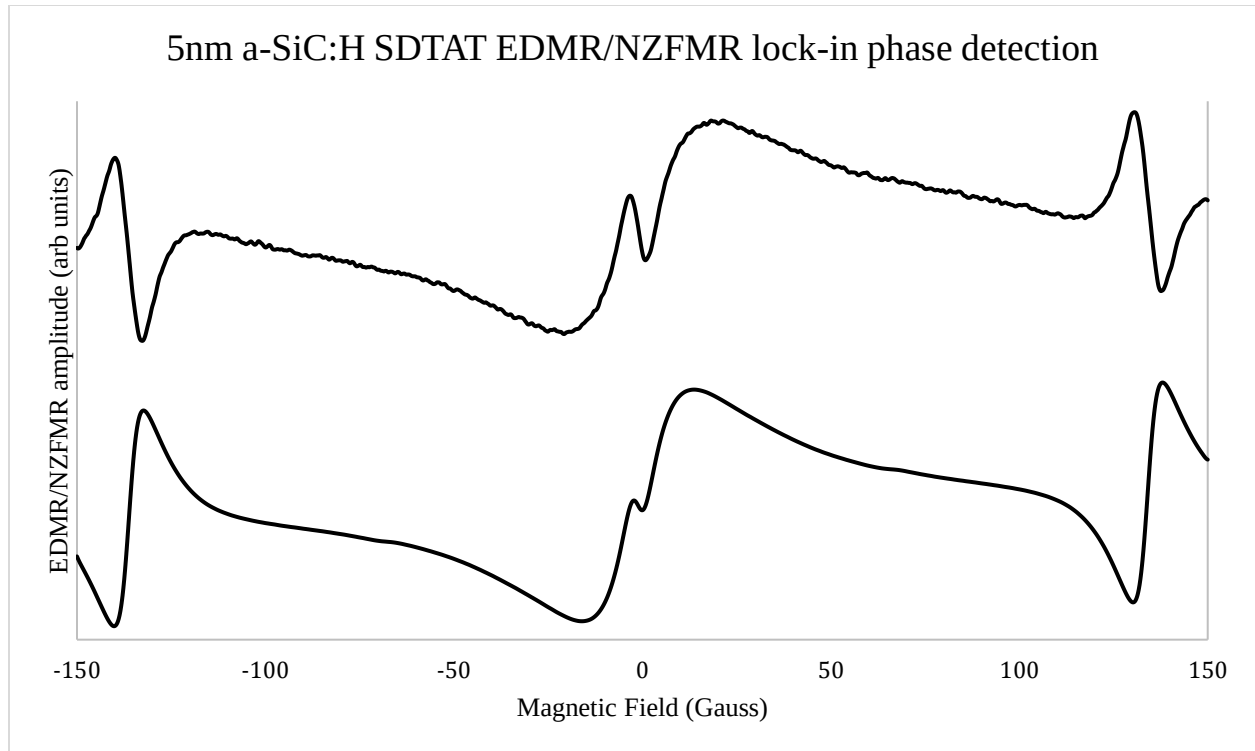


Figure 6.8: Phase shift in EDMR response in 5nm a-SiC:H relative to NZFMR response. Also note the relative size difference between the center inflection in the top and bottom trace. Measurements were made simultaneously at identical bias. Signal amplitudes are normalized to show different line shapes.

A similar response appears at X-band with two differently shaped spectra measured simultaneously under identical experimental conditions. This may be due to a less dominant conduction mechanism that has a slightly different phase response to the magnetic field modulation that is obscured by the larger signal and can be seen once the primary conduction mechanism is removed by using the correct lock-in phase. This difference is illustrated in Figure 6.9. The Lakeshore X-band spectrometer was used to perform this measurement.

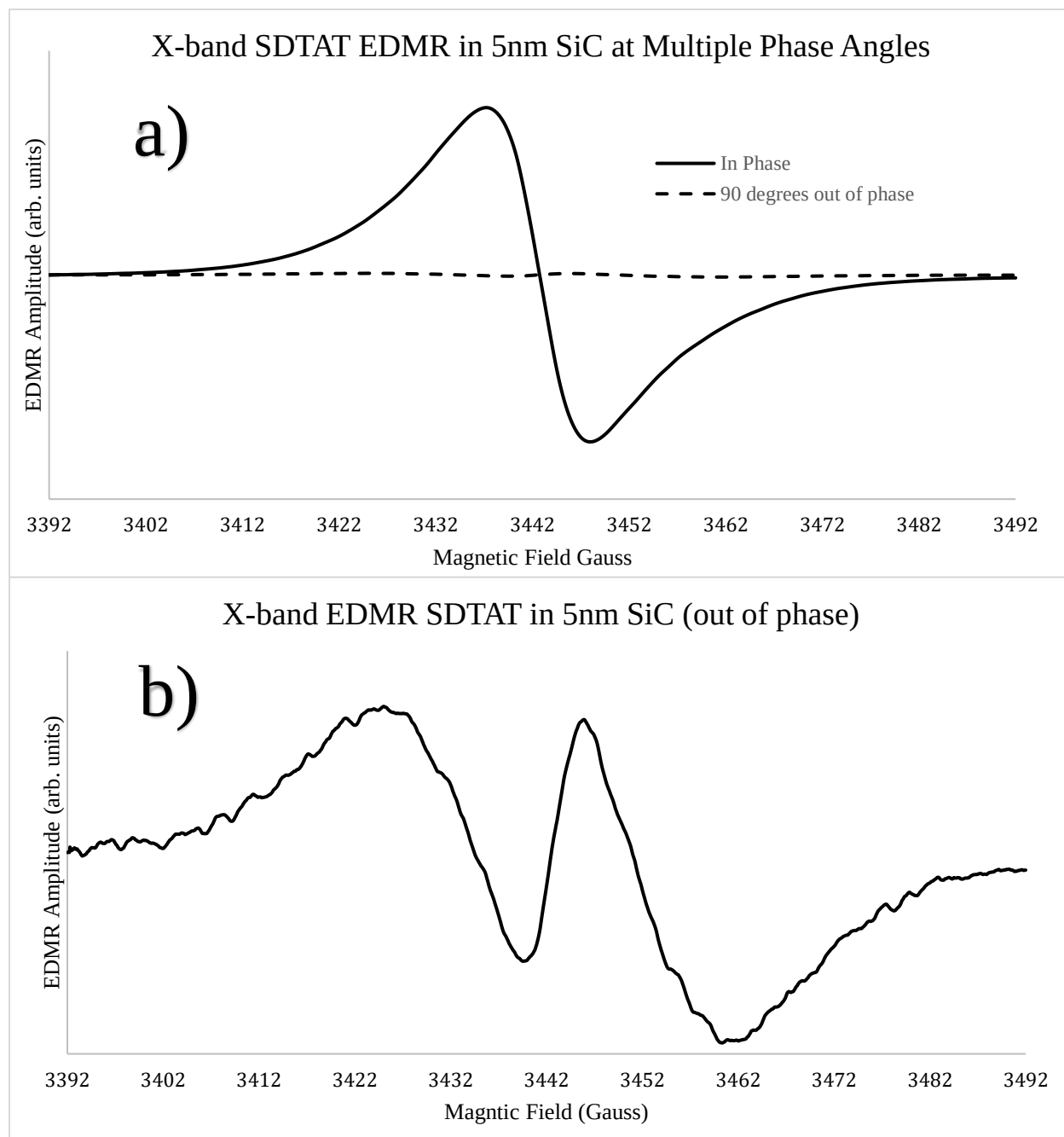


Figure 6.9: a) Relative amplitude of “in phase” vs “out of phase” SDTAT EDMR response. b) Zoomed in “out of phase” measurement in 5nm a-SiC:H, note the different shape of the EDMR response compared to the larger “in phase” response.

Chapter 6.4 Discussions about SiC, Contribution to Theory, and Future Work

The computational models for this system are still being developed, as such no direct comparisons to simulated spectra are shown. The data provided on this material in this work will, however, aid in the development of a computational model for this material system.

The SDTAT response as well as the DC current in the a-SiC:H is very stable over a wide range of biases and stressing time, unlike the amorphous carbon samples. The 5nm a-SiC:H exhibits different SDTAT NZFMR responses under different applied biases, becoming wider at higher positive bias. This would indicate that the parameters from equations 3.2.5 and 3.2.6 that change are likely r_{ea} , r_{ab} , and r_{ae} . The increased current and larger signal at higher biasing conditions would be a result of larger initial hopping rate, r_{ea} . The slight broadening of the NZFMR response with increased bias is consistent with an increase in r_{ab} . A combination of an increase in r_{ab} , and a decrease r_{ae} could also account for the approximately constant ratio the amplitude of the broad signal to that of inflection line, as the two rates changing with bias would essentially work against each other in this aspect, while allowing the broad signal to become wider.

The difference in the relative size of the center inflection in the SDTAT NZFMR response due to the lock-in detection phase may also indicate that the center inflections observed in almost all NZFMR measurements may be due to a different conduction pathway than the wider and larger signal which occurs at a slightly different phase relative to the magnetic field modulation. When combined with the changes seen in the NZFMR response in the DLC, this seems to be fairly strong evidence of each portion of the signal (the broader signal and the center inflection) arising from different pathways and spin mixing.

The SiC spin systems, for both crystalline and amorphous materials, are difficult to model as there are several spin states depending on whether a site is occupied by an electron and only certain spin transitions are allowed. [89]–[91] The spectra measured in this work will be useful for our collaborators who are focused on modelling the NZFMR phenomenon in a wider range of material systems, including different forms of SiC such as the most common and technologically relevant hexagonal 4H-SiC.

These samples offer incredibly good signal to noise ratios compared to other samples studied by the laboratory group. The simple nature of the capacitor dot samples, the simplicity of biasing scheme utilized in the measurements, and the good signal to noise ratio could allow these samples to be utilized as test samples when developing new spin-based tools and spectroscopic techniques such as the wafer probing station spectrometer outlined in appendix B.

Chapter 7

Conclusions

This study sought to develop an understanding of the atomic scale defects involved in electronic transport in amorphous carbon and amorphous silicon carbide using NZFMR and EDMR, as well as to determine the analytical power of new computational models for NZFMR.

Chapter 5 presented a variety of measurements performed on amorphous hydrogenated carbon and amorphous diamond-like carbon metal-oxide-semiconductor capacitor dots. The defect responsible for conduction in both is likely a carbon dangling bond. The a-C:H samples exhibited drastic changes to the electrical properties over time under constant biasing conditions, with the current decreasing by up two orders of magnitude over the course of several minutes. These changes in current were accompanied by trapped charge in the carbon layer. The trapped charges raise the tunneling barrier experienced by charge carriers, explaining the reduction in current. The shape of the EDMR and NZFMR spectra never changed, indicating that the electrically active defects are not changing. The line shape is also constant for different biasing conditions up to 60V. It is plausible that the trapped charges and reduced current could be symptoms of a time dependent dielectric breakdown process.

The measured NZFMR spectra were analyzed using the computational model outlined by Frantz et al. [64] to determine a number of physical parameters of the measurement. Simulated spectra were fit to the experimental data to extract hyperfine coupling constants, hopping rates, and dissociation rates. The values produced by the fitted data are physically plausible and likely correct to at least the order of magnitude. The hyperfine coupling constant could not be larger than the low field EDMR linewidth which is dominated by hyperfine interactions. The extracted hyperfine coupling constant was about 3.4 Gauss, below the 7 Gauss maximum of the low-field

EDMR linewidth and a reasonable value for nearby hydrogen. All of the parameters are of the same order of magnitude as those extracted from a recent study involving simulated spectra fitted to a spectrum for a P_b center at the Si/SiO₂ interface. [64] The hyperfine coupling constant attributed to hydrogen near a P_b center was found to be approximately 2 Gauss. Our larger value of approximately 3.4 Gauss appears to make sense given that nearby hydrogen nuclei are likely to be closer to the carbon atoms in a-C:H than the silicon atoms at the Si/SiO₂ interface, given the size difference of the respective atoms. No changes in the shape of the NZFMR spectra for different biasing conditions suggests that only the generation rate is changing, while the rest of the parameters are constant. The change in the generation rate can be attributed to the lower current due to the increased tunneling barrier caused by the trapped charge in the carbon layer. The computational model appears to be an effective tool for analyzing the a-C:H samples.

The other amorphous carbon sample, diamond-like carbon, also exhibited unstable electrical characteristics, however the changes seen in the DLC were much slower and required a larger bias to achieve. At low biasing conditions, the samples were fairly stable and simulated spectra could be fit to the experimental data to extract some physical parameters. Unlike the a-C:H, the shape of the NZFMR spectra changed with bias in the DLC samples. Simulated spectra were fitted to three experimental spectra corresponding to the lower biasing conditions of 1V, 2V, and 3V. The value for hyperfine coupling constant, 3.8 Gauss, was found to be similar to the value for the other carbon samples and less than the 9 Gauss wide low-field EDMR line width. The larger value for the DLC make sense as it has a broader low field EDMR line-width, which is likely dominated by hyperfine interactions. The hopping rate in the DLC is similar to that in the a-C:H although the changes in the line shape for increasing bias have been attributed

to a reduction in the dissociation rate, likely because more hopping can occur at higher bias. The values for this rate are also similar to the dissociation rate in the a-C:H samples.

The changes in the DLC samples over time under constant bias are different than those seen in the a-C:H samples, with the leakage current increasing over time. This change in current was accompanied by a change in the shape of the NZFMR spectra, although the signal to noise ratio of these measurements was not sufficient for fitting simulated spectra. The drastic change in the line shape indicates that another defect is likely forming in the sample and is contributing to conduction. Some progress has been made on determining the hyperfine coupling constants that could result in the changed spectra, and the best attempt so far indicates that two pathways with different hyperfine coupling constants are likely contributing to the measured spectra. The change in line shape can be achieved by adjusting the contribution of each of the pathways over time. [87] The computational model appears to be an effective tool for analyzing the DLC at low bias and will likely become more effective at higher biasing conditions as the model is developed.

Chapter 6 presented EMDR and NZFMR measurements performed on amorphous hydrogenated silicon carbide. The a-SiC:H samples were very stable over time and no changes were observed in the electrical characteristics or the EDMR/NZFMR spectra. X-band EDMR data was not enough to determine the defect responsible for conduction, however, comparing the X-band spectra with those measured at low magnetic field allowed for a value to be calculated for $\Delta g = 0.0016$. This indicates that the defect responsible for the spectra is likely a carbon dangling bond.

Computational models for SiC systems are still being developed, however, due to the potential complexity of the SiC structures [89]–[91], no simulated spectra were fitted. A

qualitative understanding of the changes to the NZFMR spectra due to bias indicates that the increased signal amplitude likely due to a larger generation rate, due to a higher overall current. The generation and dissociation rates change due to bias in manner that causes the center inflection shape to remain constant and the broad line to become wider. This is likely caused by an increase in the hopping rate and a decrease in the dissociation rate as the bias is increased. This may seem counterintuitive as one might expect the spin-independent dissociation rate to become larger at higher bias as tunneling through the thin samples becomes easier. The data collected on these model samples will be utilized to further develop the computational model in order to study and analyze other devices and material systems.

A curious phenomenon was observed in these a-SiC:H samples. A different line shape was observed for both NZFMR and EDMR measurements for different lock-in detection phases. This may be due to a separate, and much less prominent signal, that is usually obscured by the large signal. Careful selection of the lock-in detection phase allows one to essentially cut out the large signal and see the smaller one. The different pathway may also be responsible for the inflection line in the NZFMR signal as the relative amplitude of the inflection to the broad line also changes with detection phase. The large signal to noise ratio of these samples also allows them to be used when developing new spin dependent spectroscopic and measurement tools such as the spin-based magnetometer proposed by Cochrane [43].

APPENDIX A

NZFMR AND LOW FIELD EDMR IN SIGE P-MOSFETS

Silicon germanium ($\text{Si}_{1-x}\text{Ge}_x$) alloys are potentially useful materials with tunable bandgaps, depending on the concentration of each species. The bandgap can be tuned between the values for pure germanium and pure silicon, 0.66 eV and 1.1 eV respectively. The material can be easily implemented into silicon manufacturing lines and the tunability of the bandgap allows for faster heterojunction bipolar transistors and thin film CMOS transistors to be manufactured. [92]–[95] This makes SiGe alloys good candidates to be studied using spin-based spectroscopy techniques to identify the performance limiting defects in the material.

EDMR and NZFMR measurements were made on SiGe alloy p-MOSFETs with varying levels of success. Low field EDMR and NZFMR were successfully performed using the SDGP and DCIV biasing schemes, however the same measurements could not be successfully performed at X-band. Several attempts were made to boost the signal to noise ratio of the measurements at X-band including increasing the power of the microwaves in the microwave cavity and performing the measurements at low temperatures ranging from 77K to room temperature (300K). The low temperature measurements were made using liquid nitrogen in a Janis continuous flow cryostat installed into the modified commercial Bruker EDMR spectrometer used in other portions of this work. These noise reduction methods did not produce usable results at X-band and as such only low-field EDMR and NZFMR spectra are reported for the SiGe p-MOSFETs.

It is possible that the reason no spectra were observed in X-band EDMR measurements is a large spin-orbit coupling from germanium atoms, which have much higher nuclear charge (32 protons) than the silicon (14 protons) and carbon (6 protons) atoms from other measurements in

this work. As stated before, large nuclear charges increase spin-orbit coupling and can broaden EDMR signals at higher frequencies. The increased broadening of the signal due to the spin orbit coupling from germanium nuclei could widen the signal, thereby reducing the signal amplitude below the detection level of the spectrometer. Several attempts were made to signal average for more than seven days without producing recognizable spectra. One of these attempts is shown in Figure A.1.

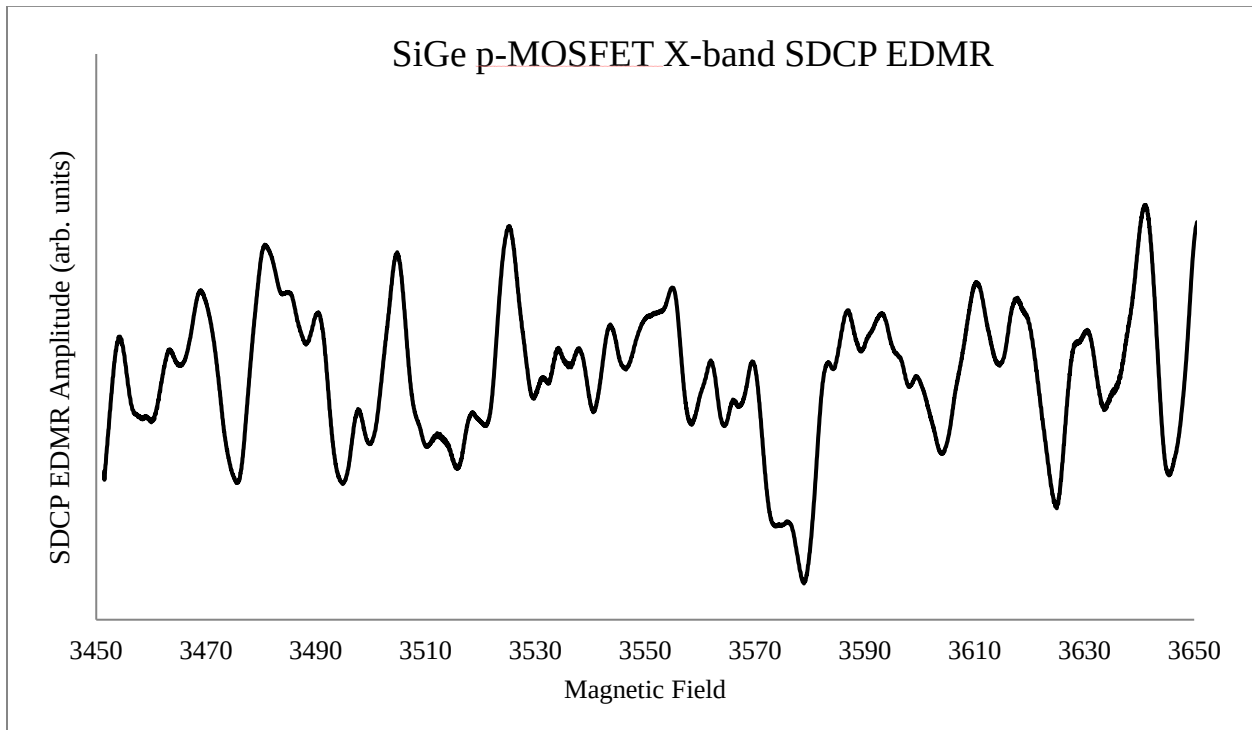


Figure A.1: X-band SDCP EDMR measurement in $\text{Si}_{0.6}\text{Ge}_{0.4}$ pMOSFET, no spectrum is measured even though extensive signal averaging was utilized. The trace was averaged 5000 times over the period of one week.

The SiGe p-MOSFET samples are epitaxial $\text{Si}_{0.6}\text{Ge}_{0.4}$ grown on silicon with effective an effective gate oxide thickness of 1.2nm. The gate area was approximately $100\mu\text{m}$ wide by $1\mu\text{m}$ long, making them ideal for charge pumping measurements. The first measurement performed on the SiGe MOSFET samples was near zero field spin dependent charge pumping (NZFSDCP).

The gate pulse used for this measurement was a 1 MHz, $1.6V_{pk-pk}$ (-.4V to 1.2V), trapezoidal waveform with rise and fall times equal to 100ns ($1/10^{th}$ of the total waveform period). This waveform was chosen to bring the interface into accumulation and inversion and the rise and fall times were chosen to provide enough time to allow free carriers at the interface to evacuate before the opposite charge carriers were brought to the interface for recombination to occur. The measured SDCP EDMR and NZFSDCP response is shown in Figure A.2.

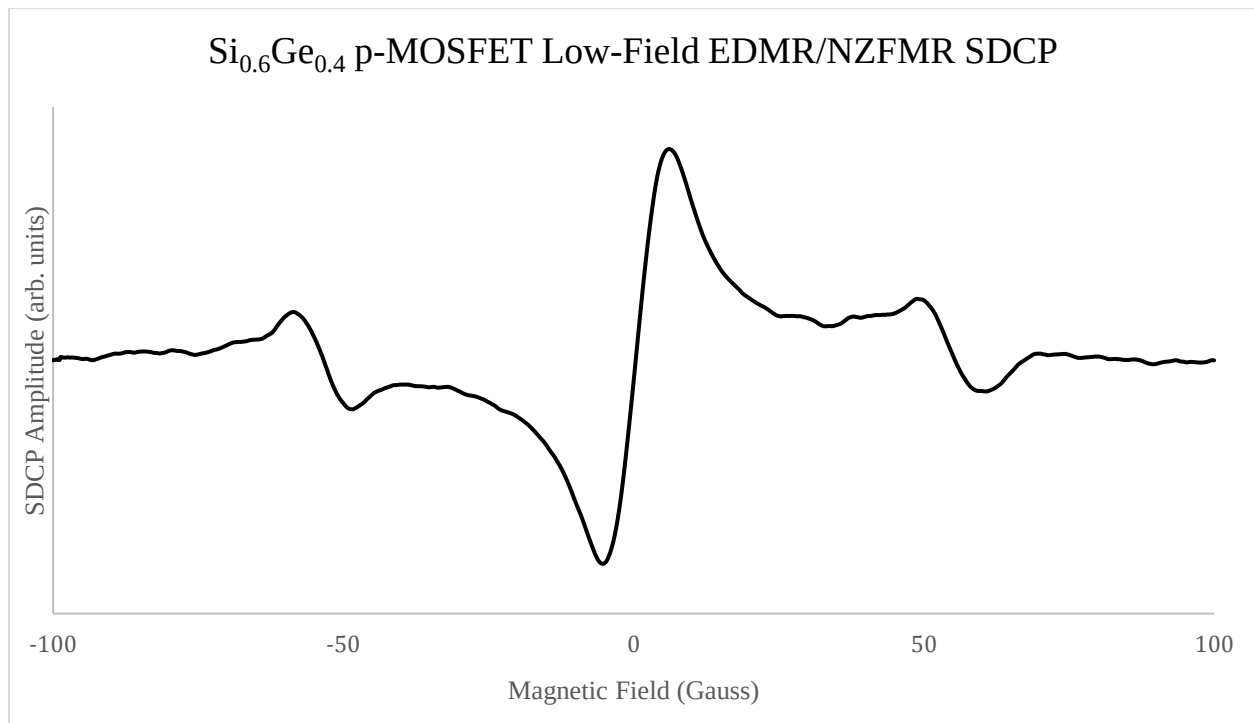


Figure A.2: Near zero field and low field EDMR spin dependent charge pumping in $Si_{0.6}Ge_{0.4}$ pMOSFET.

NZFMR was also performed on a similar sample that was biased in the DCIV scheme with the gate held at 0V and the source/drain to body bias of +0.3V. This scheme was chosen to ensure the interface was held in depletion to facilitate recombination at the interface. The signal to noise ratio of this measurement was much lower than that for the SDCP EDMR and NZFSDCP. The measured spectrum is shown in Figure A.3.

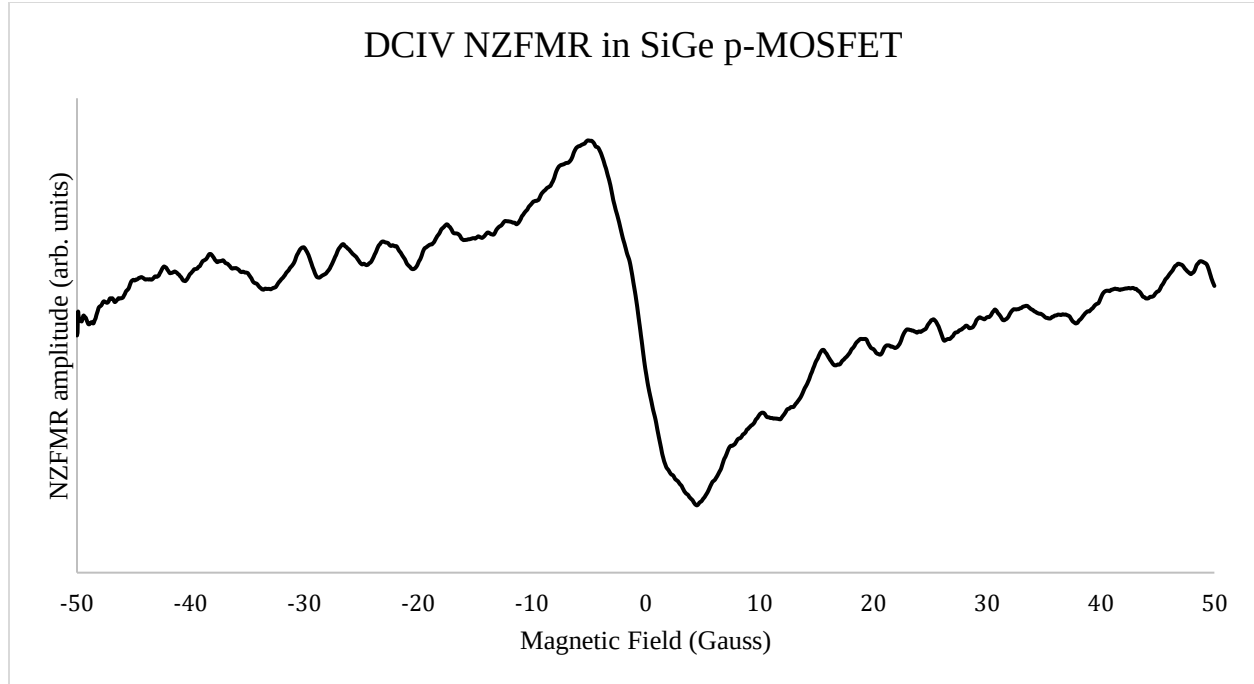


Figure A.3: DCIV NZFMR spectrum in $\text{Si}_{0.6}\text{Ge}_{0.4}$ pMOSFET.

The phase shift phenomenon seen in the a-SiC:H is also seen in the SDCP measurements in the $\text{Si}_{0.6}\text{Ge}_{0.4}$ MOSFETs where the EDMR (up-down-up) is out of phase with the NZFMR (down-up-down) as seen in Figure A.2. This phase shift makes sense as the two signals arise from very different mechanisms. Both signals occur because of a change in the singlet population of the electron spins allowing for recombination to occur; however, the EDMR response is due to electron spins flipping at resonance while the NZFMR response is due to spin mixing with nearby magnetic nuclei. It is therefore understandable why these two different mechanisms could occur at different phases relative to the modulation field phase.

APPENDIX B

SDTAT NZFMR SPECTROSCOPY IN A WAFER PROBING STATION

B.1 Construction of NZFMR Spectrometer in Wafer Probing Station

NZFMR is a simpler spectroscopic technique than EPR and EDMR; however, it typically involves quite a lot of sample preparation. Samples must be diced from their wafers and mounted onto special PCBs used to hold the sample in the electromagnet and to make electrical contact to the sample. The ability to bypass sample preparation and perform spin-based spectroscopy on samples at the wafer level would add to the speed and throughput of the technique, allowing for more samples to be studied in a shorter time. EDMR spectroscopy has been performed on a wafer probing station [96]–[98], and some forms of NZFMR, specifically SDCP, have been performed at the wafer level [99].

An apparatus similar to that proposed by Anders et al. [99] was designed and built to allow for wafer level SDTAT NZFMR on the samples studied in this work. This undertaking was initially proposed in order to better study the 500nm a-C:H due to a problem with the metal top contact having poor adhesion to the carbon film. The metal layer could be accidentally removed from the sample during wire bonding, rendering the sample essentially useless. It was decided that this problem would be addressed in two ways, the first of which was to determine a method by which the samples could be wire bonded without causing damage to the samples or the metallic contact. The second method used to address this problem was to incorporate NZFMR spectroscopy into a wafer probing station, removing the need to bond wires to the sample entirely. It was decided that the first method, determining the proper way to wire bond to the samples without causing damage to them, would be the most effective as it would allow for the samples to be studied using X-band and low field EDMR as well as NZFMR, however,

NZFMR would also be incorporated into a wafer probing station in order to determine how the technique could be improved upon.

A small electromagnet consisting of 400 turns of enamel coated magnet wire with a modulation coil consisting of 200 turns of finer gauge enamel coated magnet wire was built. The electromagnet and modulation coils were powered using components from the Blue Spin low field EDMR/NZFMR spectrometer used in other parts of this work. The applied magnetic field was measured directly using a Gaussmeter and Hall effect probe built into the Blue Spin spectrometer.

B.2 NZFMR Measurements in a Wafer Probing Station

The first NZFMR measurement on the wafer probing station was made on SiC pn-diodes that were mounted onto the PCB Ts. These samples were chosen as a good test platform for the new apparatus as they have a known and well understood spectrum and provide a very good signal to noise ratio, making them an ideal choice to test new systems. The measured SDTAT NZFMR spectra are shown in Figure B.1.

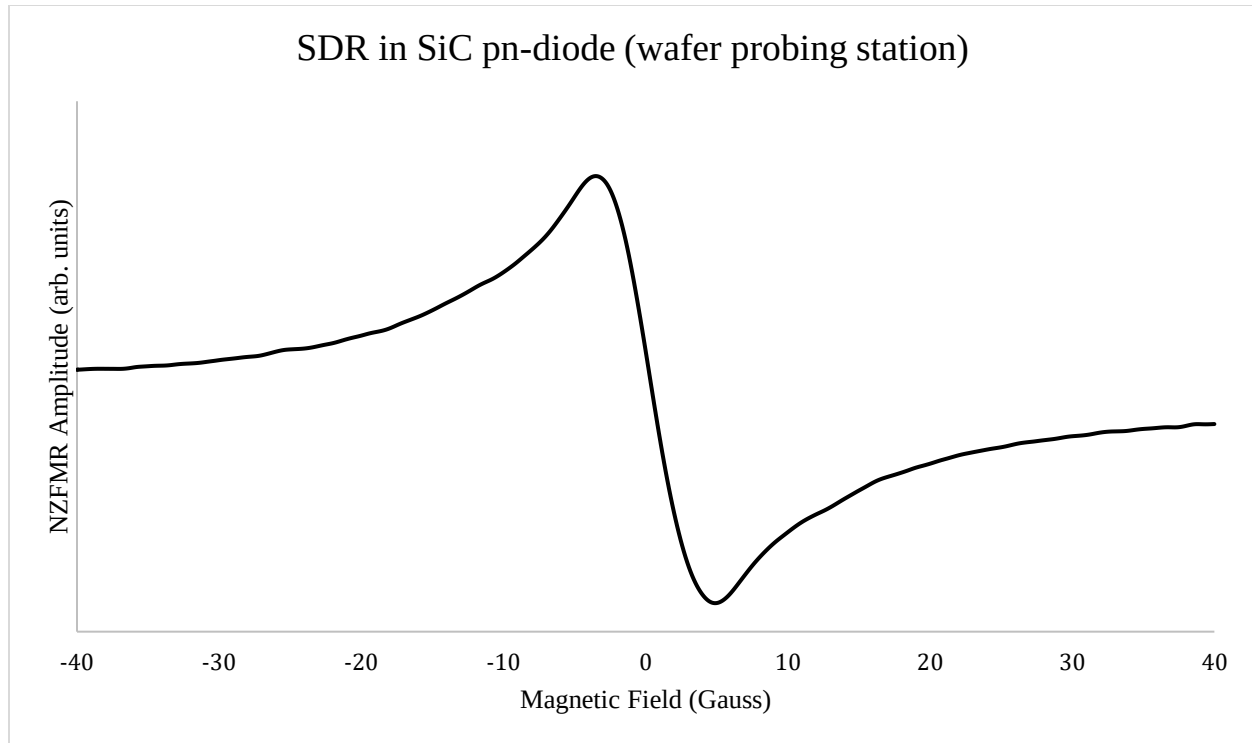


Figure B.1: SDTAT NZFMR spectrum in SiC pn-diode utilizing wafer probing station.

A 5nm a-SiC:H sample was studied using the NZFMR spectrometer incorporated into the wafer probing station. Instead of dicing the sample and mounting it to a PCB T with wire bonds for electrical connection, the sample was placed directly onto a conductive sheet of aluminum foil. The sample on the conductive sheet is shown in Figure B.2. The electromagnet used to sweep and modulate the magnetic field was removed for this image.

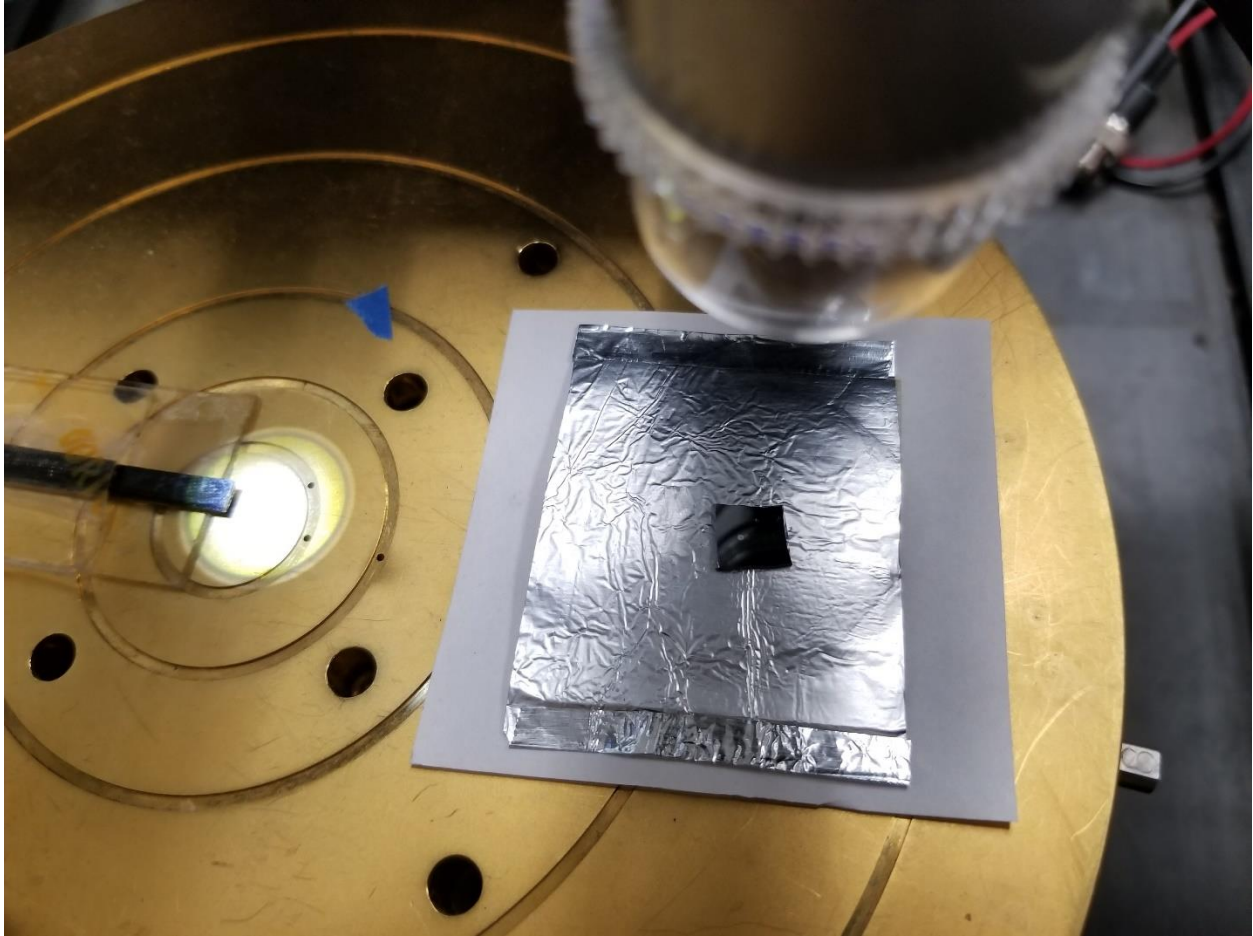


Figure B.2: 5nm a-SiC:H sample on conductive sheet with electromagnet and probe contacts removed.

Once the sample was placed onto the conductive aluminum sheet, the electromagnet was positioned such that the portion of the wafer sample under test was centered in the electromagnet. The coil for the electromagnet was wound around a 3-D printed blue PLA frame. Electrical contact was made to the sample by dropping one of the probes onto the top contact, and the other onto the conductive aluminum sheet the sample is resting on. This setup is shown in Figure B.3. Note that this portion of wafer was not diced for this measurement. There are two usable capacitors on this portion of wafer and the total sample size is approximately 1.5cm by 1.5cm, much larger than the samples used in the traditional EDMR and NZFMR spectrometers.

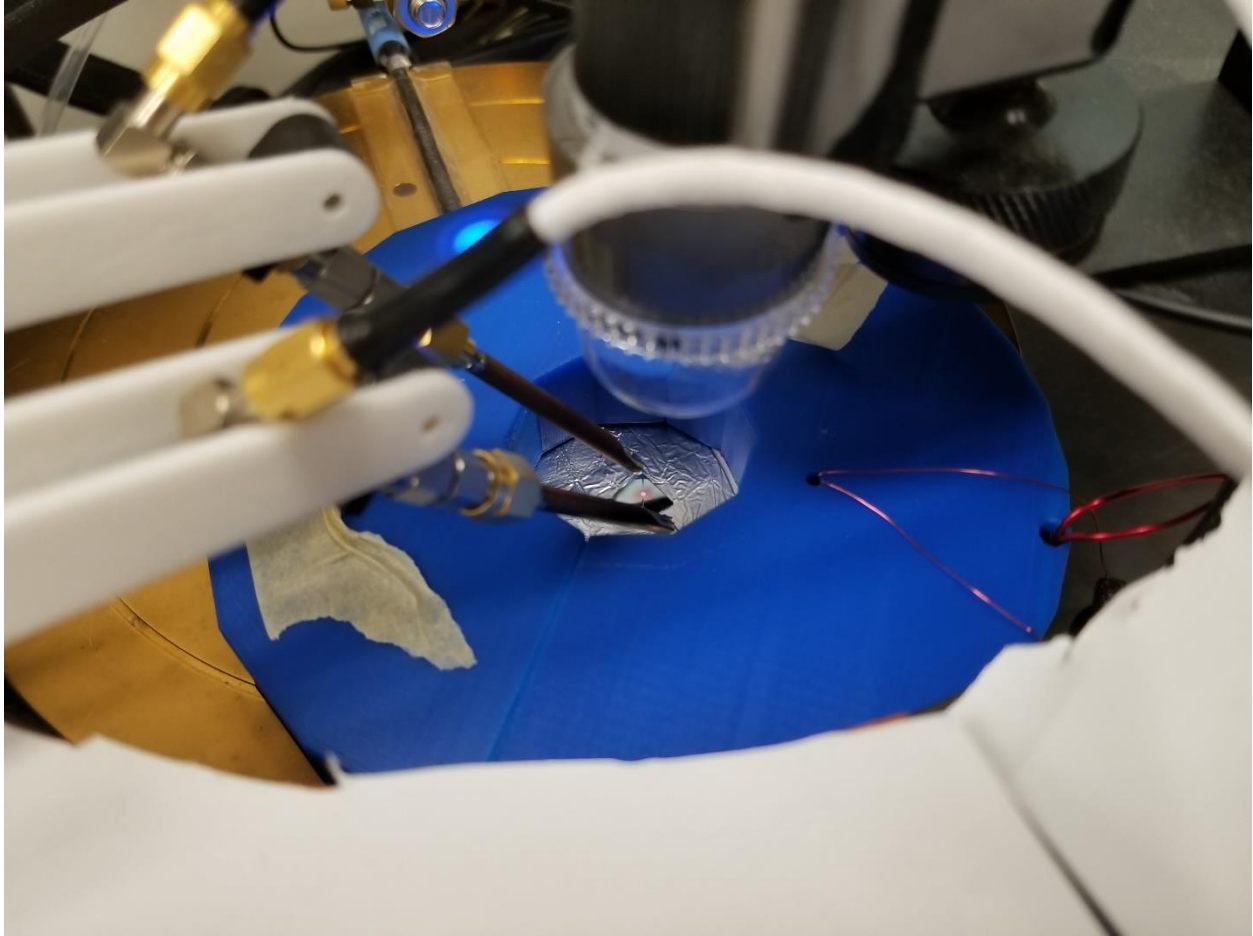


Figure B.3: 5nm a-SiC:H sample in NZFMR spectrometer electromagnet with electrical contact made using probes pictured. A digital microscope was used to ensure proper contact was made. Electrical contact to the back of the sample was made by contacting the conductive aluminum sheet.

The sample was biased at +3V and NZFMR was measured using a magnetic field modulation with an amplitude of 5 Gauss at 1000Hz. The measured spectrum has a very good signal to noise ratio and is shown in Figure B.4 alongside an NZFMR spectrum measured on a similar sample in a traditional spectrometer in which the sample had to be diced and mounted onto a PCB T. The conductive aluminum sheet was later replaced with a conductive copper sheet in order to reduce the series resistance of the measurement. The spectra are very similar

and the slight discrepancies can most likely be attributed to slight non-uniformities that arise due to the small nature of the single coil electromagnet used in wafer level system.

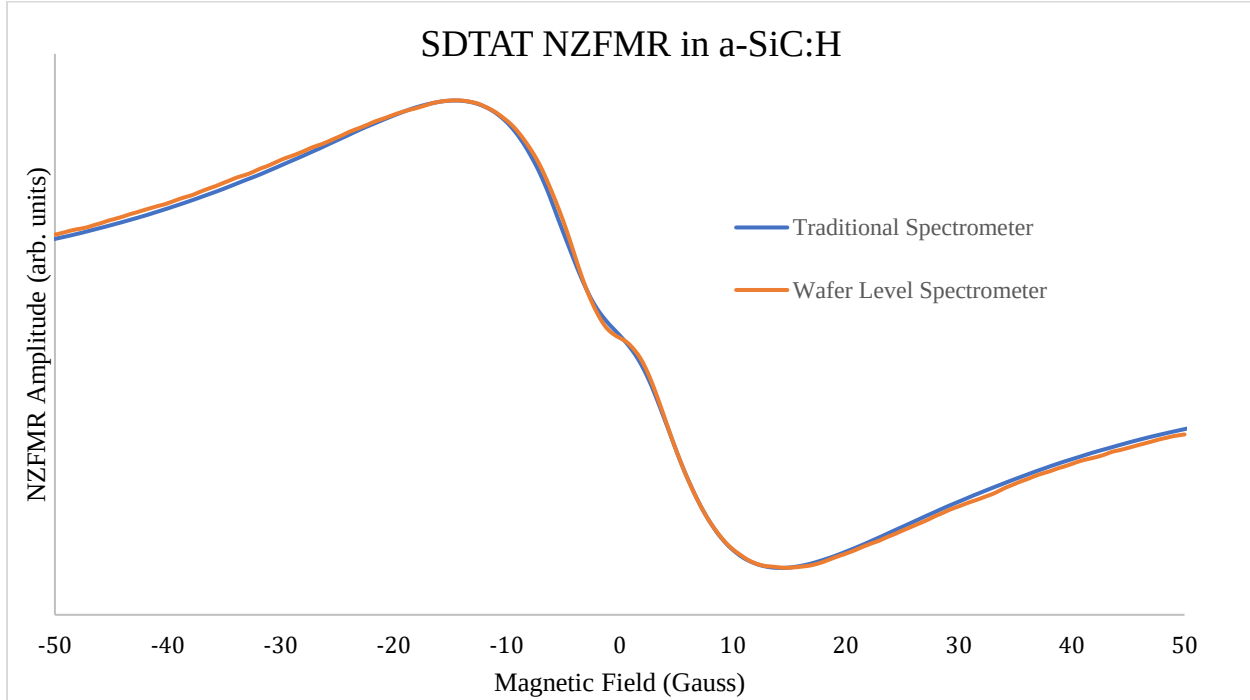


Figure B.4: SDTAT NZFMR spectra in wafer level and traditional spectrometers. The measurements were made under an applied bias of +3V using a magnetic field modulation of 5 Gauss at 1kHz.

This wafer level system looks promising for future work allowing more samples to be studied in a non-destructive manner. The faster data acquisition and higher throughput will allow for more data to be acquired in order to inform the development of computation models for NZFMR and potentially EDMR, as the system could easily be modified to include an RF resonator which would provide the B_1 oscillating magnetic field needed for EDMR. Implementing these spectroscopic techniques into wafer probing stations would allow for these very powerful techniques to be applied to the study of more samples with different materials, and devices of different architectures in both academic and industrial research settings.

APPENDIX C

SDTAT NZFMR MATLAB CODES

Primary Code Used to Simulate Spectra

This code was written by me, utilizing functions written by Elias Frantz for the SDTAT NZFMR modified two site model discussed in Chapter 3. For best results, convert file into MATLAB Live Script.

```
%% SDTAT NZFMR Simulation MATLAB Code

%{
This section of code was written by Colin McKay
This code utilizes simulation functions written by Elias Frantz
%}
%% Initial Variables, Run First

% initialization
clear
clc

% -100 Gauss to 100 Gauss (10mT =100 Gauss
Field= linspace(-10,10,4096)'; %Units: [mT]

% g value of free electron
g= 2.0023; %Units: []

% These are the variables used, the default values are given here
% HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
% HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
% r_ab= 1; %Units: [GHz]
% r_ae= 0.1; %Units: [GHz]
% r_ea= 1; %Units: [GHz]

f=0;
font='Cambria Math'; % changes font on plots

% Changes title text on plots
% will take form:
% 'Simulated NZFMR Spectra (Vary 'variable')
TextString='Simulated NZFMR Spectra (Vary ' ;

% adds 'Normalized ' to the start of the titles for normalized spectra
Normalized='Normalized ' ;

normalizedYlim=1.2; % y axis limits on normalized data
narrowXlim=20; % x axis limits on narrow plots when needed
```

```

%% Changing r_ab

% Variable Initialization
Variable='r_{\alpha\beta}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=.4:.4:2;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on
var=" ";
for i=1:length(x)
    r_ab= x(i);
    I_ab(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);
    if i==1
        I_aboffset(:,1)=I_ab(:,1);
    elseif i>1
        offset=(min(I_aboffset(:,i-1))-max(I_ab(:,i))-.001); % tries to
optimize offsets but this is easily changeable
        I_aboffset(:,i)=I_ab(:,i) + offset;
    else
    end
    plot(Field.*10,I_aboffset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var, 'FontName',font)
legend boxoff
titletext=[TextString, Variable, ' '];
title(titletext, 'FontName',font)
xlabel('Magnetic Field (Gauss)', 'FontName',font)
ylabel('Simulated NZFMR Amplitude (arb. units)', 'FontName',font)
yticks('')
% This one works on its own
% ytop=;
% ybot=;
% ylim([-1*normalizedYlim normalizedYlim])

% Calculates normalized data, both Broad and Inflection
% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_ab(:,i));

```

```

        scale1_ab(:,i)=I_ab(:,i)./pks(1); % Scales to broad signal, same as in
later portions of code
        scale2_ab(:,i)=I_ab(:,i)./pks(2); % Scales to narrow signal, same as in
later portions of code
        plot(Field.*10,scale1_ab(:,i))
end
legend(var,'FontName',font)
legend boxoff
titletext=['a) ', Normalized, TextString, Variable, ' '];
title(titletext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)
ylabel('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.3732 0.4036],[0.2929 0.8119])
annotation('textarrow',[0.375 0.5661],[0.281 0.1929],'String','Normalized
Peaks','FontName',font)

% Normalizes to Narrow line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    plot(Field.*10,scale2_ab(:,i))
end
legend(var,'FontName',font)
legend boxoff
titletext=['b) ', Normalized, TextString, Variable, ' '];
title(titletext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)
ylabel('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.4232 0.5125],[0.3167 0.8214])
annotation('textarrow',[0.4268 0.4893],[0.2786 0.1976],'String','Normalized
Peaks','FontName',font)

%% Changing r_ae

% Variable Initialization
Variable='r_{\alpha e}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=.04:.04:.2;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on

```

```

var=" ";
for i=1:length(x)
    r_ae= x(i);
    I_ae(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);
    if i==1
        I_aeoffset(:,1)=I_ae(:,1);
    elseif i>1
        offset=(min(I_aeoffset(:,i-1))-1.1*max(I_ae(:,i))); % tries to
optimize offsets but this is easily changeable
        I_aeoffset(:,i)=I_ae(:,i) + offset;
    else
    end
    plot(Field.*10,I_aeoffset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var,'FontName',font)
legend boxoff
titledtext=[TextString, Variable, ' '];
title(titledtext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)
ylabel ('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ytop=max(I_aeoffset(:,1))+.003;
ybot=min(I_aeoffset(:,end))-.001;
ylim([ybot ytop])

% Calculates normalized data, both Broad and Inflection
% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_ae(:,i));
    scale1_ae(:,i)=I_ae(:,i)./pks(1);
    scale2_ae(:,i)=I_ae(:,i)./pks(2);
    plot(Field.*10,scale1_ae(:,i))
end
legend(var,'FontName',font)
legend boxoff
titledtext=['a) ', Normalized, TextString, Variable, ' '];
title(titledtext,'FontName',font)
xlabel('Magnetic Field (Gauss)')
ylabel ('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.3946 0.4125],[0.3905 0.8357])
annotation('textarrow',[0.4071 0.5982],[0.3476 0.1881],'String','Normalized
Peaks','FontName',font)

% Normalizes to Narrow line
f=f+1;
figure (f)
clf
hold on

```

```

for i=1:length(x)
    plot(Field.*10,scale2_ae(:,i))
end
legend(var,'FontName',font)
legend boxoff
titletext=['b) ', Normalized, TextString, Variable, ' '];
title(titletext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)
ylabel ('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.375 0.5125],[0.4024 0.8357])
annotation('textarrow',[0.3857 0.4911],[0.3643 0.1929],'String','Normalized
Peaks','FontName',font)

%% Changing r_ea

% Variable Initialization
Variable='r_{e\alpha}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=0.4:.4:2;
r_ab=.3;
r_ae=.1;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on
var=" ";
for i=1:length(x)
    r_ea= x(i);
    I_ea(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);
    if i==1
        I_eaoffset(:,1)=I_ea(:,1);
    elseif i>1
        offset=(min(I_eaoffset(:,i-1))-(1.1*max(I_ea(:,i))))); % tries to
optimize offsets but this is easily changeable
        I_eaoffset(:,i)=I_ea(:,i) + offset;
    else
    end
    plot(Field.*10,I_eaoffset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var,'FontName',font)
legend boxoff
titletext=[TextString, Variable, ' '];
title(titletext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)

```

```

ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ytop=max(I_eaoffset(:,1))+.07;
ybot=min(I_eaoffset(:,end))-.01;
ylim([ybot ytop])

% Calculates normalized data, both Broad and Inflection
% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_ea(:,i));
    scale1_ea(:,i)=I_ea(:,i)./pks(1);
    if i==1
        scale1_eaOffset(:,1)=scale1_ea(:,1);
    elseif i>1
        offset=-.03*(i-1);
        scale1_eaOffset(:,i)=scale1_ea(:,i) + offset;
    else
    end
    %scale2_ea(:,i)=I_ea(:,i)./pks(2); %perfect match, not needed
    plot(Field.*10,scale1_eaOffset(:,i))
end
legend(var, 'FontName', font)
legend boxoff
titletext=[Normalized, TextString, Variable, ''];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])

%% Changing HF1

% Variable Initialization
Variable='HF_{\alpha}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 0; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=.4:.4:2;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on
var=" ";
for i=1:length(x)
    HF1= x(i);
    I_HF1(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);

```

```

    if i==1
        I_HF1offset(:,1)=I_HF1(:,1);
    elseif i>1
        offset=(min(I_HF1offset(:,i-1))-(1.1*max(I_HF1(:,i)))); % tries to
optimize offsets but this is easily changeable
        I_HF1offset(:,i)=I_HF1(:,i) + offset;
    else
    end
    plot(Field.*10,I_HF1offset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var, 'FontName', font)
legend boxoff
titletext=[TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ytop=max(I_HF1offset(:,1))+.0025;
ybot=min(I_HF1offset(:,end))-.0005;
ylim([ybot ytop])

% Calculates normalized data, both Broad and Inflection
% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_HF1(:,i));
    scale1_HF1(:,i)=I_HF1(:,i)./pks(1);
    try
        scale2_HF1(:,i)=I_HF1(:,i)./pks(2);
    catch
        disp('Only 1 peak')
        scale2_HF1(:,i)=I_HF1(:,i)./pks(1);
    end
    plot(Field.*10,scale1_HF1(:,i))
end
legend(var)
legend boxoff
titletext=['a) ', Normalized, TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.3911 0.4125],[0.3071 0.7857])
annotation('textarrow',[0.4 0.5643],[0.2905 0.1881],'String','Normalized
Peaks','FontName',font)

% Normalizes to Narrow line
f=f+1;
figure (f)
clf

```

```

hold on
for i=2:length(x)
    plot(Field.*10,scale2_HF1(:,i))
end
legend(var(2:end))
legend boxoff
titletext=['b) ', Normalized, TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
xlim([-1*narrowXlim narrowXlim])
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow', [0.3339 0.6036], [0.1881 0.8071])
annotation('textarrow', [0.3357 0.4268], [0.169 0.1643], 'String', 'Normalized
Peaks', 'FontName', font)

%% Changing HF2

% Variable Initialization
Variable='HF_{\beta}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=.4:.4:2;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on
var=" ";
for i=1:length(x)
    HF2= x(i);
    I_HF2(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);
    if i==1
        I_HF2offset(:,1)=I_HF2(:,1);
    elseif i>1
        offset=(min(I_HF2offset(:,i-1))-(1.1*max(I_HF2(:,i))))); % tries to
optimize offsets but this is easily changeable
        I_HF2offset(:,i)=I_HF2(:,i) + offset;
    else
    end
    plot(Field.*10,I_HF2offset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var, 'FontName', font)
legend boxoff
titletext=[TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)

```

```

ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ytop=max(I_HF2offset(:,1))+.003;
ybot=min(I_HF2offset(:,end))-.0005;
ylim([ybot ytop])

% Calculates normalized data, both Broad and Inflection
% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_HF2(:,i));
    scale1_HF2(:,i)=I_HF2(:,i)./pks(1);
    try
        scale2_HF2(:,i)=I_HF2(:,i)./pks(2);
    catch disp('Only 1 peak')
    end
    plot(Field.*10,scale1_HF2(:,i))
end
legend(var, 'FontName', font)
legend boxoff
titletext=['a) ', Normalized, TextString, Variable, ' ');
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.35 0.4107],[0.2905 0.8071])
annotation('textarrow',[0.3536 0.5821],[0.2714 0.1881], 'String', 'Normalized
Peaks', 'FontName', font)

% Normalizes to Narrow line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    plot(Field.*10,scale2_HF2(:,i))
end
legend(var, 'FontName', font)
legend boxoff
titletext=['b) ', Normalized, TextString, Variable, ' ');
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
xlim([-1*narrowXlim narrowXlim])
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow',[0.3464 0.5804],[0.3405 0.8048])
annotation('textarrow',[0.3643 0.4482],[0.2976 0.2119], 'String', 'Normalized
Peaks', 'FontName', font)

%% Changing HF1 and HF2 together

```

```

% Variable Initialization
Variable='HF_{\alpha} and HF_{\beta}';
HF1= 1; %Units: [mT] %Hyperfine interaction strength at Site 1
HF2= 1; %Units: [mT] %Hyperfine interaction strength at Site 2
r_ab= 1; %Units: [GHz]
r_ae= 0.1; %Units: [GHz]
r_ea= 1; %Units: [GHz]

% Variable values, define in any way you want
x=.4:.4:2;

% Calculates and plots the raw spectra with offsets
f=f+1;
figure (f)
clf
hold on
var=" ";
for i=1:length(x)
    HF1= x(i);
    HF2= x(i);
    I_HF12(:,i)= SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea);
    if i==1
        I_HF12offset(:,1)=I_HF12(:,1);
    elseif i>1
        offset=(min(I_HF12offset(:,i-1))-(1.1*max(I_HF12(:,i)))); % tries to
optimize offsets but this is easily changeable
        I_HF12offset(:,i)=I_HF12(:,i) + offset;
    else
    end
    plot(Field.*10,I_HF12offset(:,i))
    text=string(num2str(x(i)));
    var(i)=text;
end
legend(var,'FontName',font)
legend boxoff
titletext=[TextString, Variable, ' '];
title(titletext,'FontName',font)
xlabel('Magnetic Field (Gauss)','FontName',font)
ylabel ('Simulated NZFMR Amplitude (arb. units)','FontName',font)
yticks('')
ytop=max(I_HF12offset(:,1))+.005;
ybot=min(I_HF12offset(:,end))-.0005;
ylim([ybot ytop])

% Normalizes to Broad line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    [pks,locs]=findpeaks(I_HF12(:,i));
    scale1_HF12(:,i)=I_HF12(:,i)./pks(1);
    scale2_HF12(:,i)=I_HF12(:,i)./pks(2);
    plot(Field.*10,scale1_HF12(:,i))
end

```

```

legend(var, 'FontName', font)
legend boxoff
titletext=['a] ', Normalized, TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow', [0.3768 0.3893], [0.269 0.8071])
annotation('textarrow', [0.3875 0.5643], [0.2476 0.2], 'String', 'Normalized
Peaks', 'FontName', font)

% Normalizes to Narrow line
f=f+1;
figure (f)
clf
hold on
for i=1:length(x)
    plot(Field.*10, scale2_HF12(:, i))
end
legend(var, 'FontName', font)
legend boxoff
titletext=['b] ', Normalized, TextString, Variable, ' '];
title(titletext, 'FontName', font)
xlabel('Magnetic Field (Gauss)', 'FontName', font)
ylabel ('Simulated NZFMR Amplitude (arb. units)', 'FontName', font)
yticks('')
xlim([-1*narrowXlim narrowXlim])
ylim([-1*normalizedYlim normalizedYlim])
annotation('arrow', [0.3554 0.5732], [0.2214 0.8167])
annotation('textarrow', [0.3554 0.4643], [0.2071 0.2], 'String', 'Normalized
Peaks', 'FontName', font)

```

Functions Needed to Run Primary Code

The primary code used to simulate the SDTAT NZFMR spectra in this study calls upon four functions written by Elias Frantz for the SDTAT NZFMR simulation code referenced in chapter 3. The four function names are “DiracDelta”, “Pauli”, “SpectraProducer”, and “SpinSystem”. To use these codes together, save each function into its own .m file named with the exact case sensitive characters inside the quotations marks in the section heading.

“DiracDelta” Function

```

function [Out] = DiracDelta(m,n)
%DiracDelta is a numeric equivalent of the MATLAB built in: kroneckerDelta.
% [Out] = DiracDelta(m,n)
if m==n

```

```

        Out= 1;
else
        Out= 0;
end
end

```

“Pauli” Function

```

function [Out] = Pauli(Spin,xyz)
%Pauli2 creates a Pauli spin matrix (vector) given a given Spin
(S=1/2,S=1,S=3/2,...) and
%the vector direction (x,y, or z).
% [Out] = Pauli2(Spin,xyz)
iterations= 2*Spin+1;
m= linspace(-Spin,Spin,iterations);
Out= zeros(iterations,iterations);
switch xyz
    case 1
        for j= 1:iterations
            for k= 1:iterations
                Out(j,k)= (DiracDelta(j,k+1) +
DiracDelta(j+1,k))*0.5*sqrt((Spin*(Spin+1)-m(j)*m(k)));
            end
        end
    case 2
        for j= 1:iterations
            for k= 1:iterations
                Out(j,k)= (DiracDelta(j,k+1) -
DiracDelta(j+1,k))*0.5i*sqrt((Spin*(Spin+1)-m(j)*m(k)));
            end
        end
    case 3
        for j= 1:iterations
            for k= 1:iterations
                Out(j,k)= -DiracDelta(j,k)*m(j);
            end
        end
end
end
end

```

“SpectraProducer” Function

```

function [I] = SpectraProducer(Field,g,HF1,HF2,r_ab,r_ae,r_ea)
%PassSpectraFit is passed into fminsearch to extract the
%spectroscopic components of the NZFMR Spectra.
% [I] = SpectraProducer(Field,NuclearSpin,g,HyperfineValue,ks,kd,Gen,I0)
%% Conditions for fminsearch
HF1= abs(HF1);
HF2= abs(HF2);
ks1= abs(r_ab);
kd1= abs(r_ae);
Gen1= abs(r_ea);

```

```

%% Spin System
[sx,sy,sz]= SpinSystem([1/2,1/2,1/2,1/2]);
%% Spin Operators
S_tot= sz{1}+sz{2};
% Electron-Electron Spin Product Projection Operators
S1S2= sx{1}*sx{2} + sy{1}*sy{2} + sz{1}*sz{2};
% Electron-Nuclear Spin Product Projection Operators
IS1= sx{3}*sx{1} + sy{3}*sy{1} + sz{3}*sz{1};
IS2= sx{4}*sx{2} + sy{4}*sy{2} + sz{4}*sz{2};
% Singlet & Triplet Projection Operators
Ident= eye(size(S1S2));
Ps= (1/4)*( Ident-4*S1S2);
Pt= (1/4)*(3*Ident+4*S1S2);
%% Constants
uB= 5.788e-8; %eV/mT
h_bar= 6.582E-7; %eV*ns
%% Hamiltonians + Solve
Hhf1= g*uB*HF1*IS1 + g*uB*HF2*IS2;
I1= zeros(length(Field),1);
G1= (1/16)*Gen1*Ident;
for k= 1:length(Field)
    B0= Field(k)-0.037851;
    H01= g*uB*B0*(S_tot);
    H_NZFMR1= H01 + Hhf1;
    A= (-(1i)/h_bar)*H_NZFMR1-(ks1/2)*Ps-(kd1/2)*Pt;
    B= ((1i)/h_bar)*H_NZFMR1-(ks1/2)*Ps-(kd1/2)*Pt;
    P1= lyap(A,B,G1);
    I1(k,1)= (kd1/ks1).*real(trace(Ps*P1));
end
I1= I1-I1(1);
I= gradient(I1)./gradient(Field);
end

```

“SpinSystem” Function

```

function [sx,sy,sz] = SpinSystem(spins)
%SpinSystem creates cell arrays of sx, sy, and sz in the appropriate spin
%bases given a vector of nuclear spins.
% [sx,sy,sz] = SpinSystem(spins)
iterations= length(spins);

spinMat= [];
for l= 1:iterations
    spinMat= vertcat(spinMat,spins);
end

spinCellx{iterations,iterations}= [];
spinCelly{iterations,iterations}= [];
spinCellz{iterations,iterations}= [];

for m= 1:iterations
    for n= 1:iterations
        if n==m
            spinCellx{m,n}= Pauli(spinMat(m,n),1);

```

```

        spinCelly{m,n}= Pauli (spinMat (m,n) ,2);
        spinCellz{m,n}= Pauli (spinMat (m,n) ,3);
    else
        spinCellx{m,n}= eye (size (Pauli (spinMat (m,n) ,1)));
        spinCelly{m,n}= eye (size (Pauli (spinMat (m,n) ,2)));
        spinCellz{m,n}= eye (size (Pauli (spinMat (m,n) ,3)));
    end
end
end

sx{iterations,1}= [];
sy{iterations,1}= [];
sz{iterations,1}= [];

for j= 1:iterations
    x= spinCellx{j,1};
    y= spinCelly{j,1};
    z= spinCellz{j,1};
    for k= 2:iterations
        x= kron(x,spinCellx{j,k});
        y= kron(y,spinCelly{j,k});
        z= kron(z,spinCellz{j,k});
    end
    sx{j,1}= x;
    sy{j,1}= y;
    sz{j,1}= z;
end
end

```

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