MAGNETIC RESONANCE AND MAGNETORESISTANCE FOR THE
UNDERSTANDING OF DEFECT CHEMISTRY AND SPIN-TRANSPORT IN
AMORPHOUS SEMICONDUCTORS AND DIELECTRICS

A Dissertation in
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by

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Abstract

Amorphous semiconductors and dielectrics are widely utilized throughout the microelectronics industry. Applications include thin-film transistors (TFTs) utilized in flat panel displays and solar cells, oxides in metal-oxide-semiconductor field-effect transistors (MOSFETs) for microprocessors and memory-cell access devices, low-dielectric constant (κ) interlayer dielectrics which separate back-end of line interconnects, and several others. Like other systems, reducing performance limiting defects within amorphous systems is critical for microelectronic integrated circuit (IC) development and improvement. Perhaps the most powerful analytical tool for studying point defects in electronic materials is electron paramagnetic resonance (EPR). However, EPR is not sensitive enough to measure defects in state-of-the-art microelectronic devices, since its sensitivity is limited to \(10^{10}\) total defects. Additionally, EPR spectra of defects within amorphous systems often are often featureless due to the inherent disorder of these systems. This work utilizes an EPR-based approach, electrically detected magnetic resonance (EDMR), to study defect chemistry in amorphous semiconductors and dielectrics even when featureless spectra are present. EDMR is the electrically detected analog of EPR in which EPR induced changes in device current are detected. In this study, EDMR is detected via changes in amorphous semiconductor or dielectric tunneling current via spin-dependent trap assisted tunneling (SDTAT) events. Due to the nature of SDTAT, defects detected are directly linked to electronic transport; an additional benefit of EDMR relative to EPR. Unlike EPR, SDTAT/EDMR may also be detected at any field/frequency combination without loss of sensitivity. As will be explained, this field/frequency independence allows for a distinction between EDMR line width contributions from electronic g tensor components or electron-
nuclear hyperfine interactions, thus providing insight into defect chemistry when featureless spectra are present. Additionally, performing EDMR measurements at multiple biases and comparing with MIS band diagrams allows for a rudimentary understanding of defect energy levels. Finally, we utilize EDMR to understand near-zero-field magnetoresistance (MR) phenomena, which are of interest for spin-transport applications such as spin-valves and magnetometers.

The EDMR techniques utilized in this study are relatively new, and have not been exploited to study a wide range of electronic materials. Thus, in Chapter 4, baseline EDMR measurements are provided in relatively simple amorphous systems including a-Si:H and a-C:H. We find that EDMR spectra in a-Si:H and a-C:H systems are due to silicon and carbon dangling bonds, respectively. Additionally, we utilize multiple frequency EDMR to provide additional information regarding contributions of line width due to the breadth of $g$ tensor components in the featureless a-Si:H and a-C:H EDMR spectra. By providing a measurement of $g$ tensor breadth, $\Delta g$, we develop a baseline for distinguishing between silicon and carbon dangling bonds in more complex systems, such as low-$\kappa$ dielectrics a-SiOC:H and a-SiCN:H, in which silicon and/or carbon dangling bonds may be present.

Low-$\kappa$ dielectric constant materials are critical for reducing parasitic capacitances due to the scaling of back-end of line interconnects. In Chapter 4, we first utilize conventional EPR measurements to study a variety of porous low-$\kappa$ dielectric powders. Via conventional EPR on these low-$\kappa$ powders, we are able to analyze the effects of UV radiation and remote hydrogen plasma upon the low-$\kappa$ systems. Our results indicate that UV treatments, which are utilized to eliminate sacrificial porogens to introduce pores, significantly increase defect density. Remote hydrogen plasma (RHP) treatments are found
to decrease dangling bond concentration. However, due to the featureless EPR spectra, we are unable to provide insight into defect chemistry via conventional EPR. Thus, we utilize multiple field/frequency EDMR in these low-κ systems, and compare Δg measurements with previous baseline measurements, to provide insight into defect chemistry which was previously unavailable. We find a multitude of silicon and carbon dangling bonds in a-SiOCH and a-SiCN:H dielectrics. Defect chemistry seems to depend upon precursor chemistry. Additionally, EDMR measurements confirm that UV treatments in low-κ systems introduce silicon dangling bonds, suggesting that these treatments may be damaging the Si-O-Si network in a-SiOC:H systems. Finally, we perform EDMR measurements at multiple biases to get a general understanding of defect energy levels in these systems. Band gaps are calculated via reflected electron energy loss spectroscopy (REELS), and band offsets are calculated via X-ray photoelectron spectroscopy (XPS). We find that carbon dangling bonds in a-SiOC:H systems have levels near the middle of the a-SiOC:H band gap, and silicon dangling bonds in a-SiCN:H systems have levels near the upper-middle part of the a-SiCN:H band gap.

In Chapter 5, we analyze silicon nitride (a-SiN:H) thin films, which are widely utilized in the electronics industry as gate dielectrics for TFTs. However, defects and electronic transport in these systems are not fully understood. We utilize multiple frequency EDMR and variable bias EDMR to better understand defect chemistry and energy levels in a-SiN:H systems. It is found that K centers, which have been previously observed in a-SiN:H via EPR and electron nuclear double resonance (ENDOR), are primarily responsible for transport in these systems. Additionally, we find that K centers
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In Chapter 6, we illustrate that near-zero field MR phenomena are ubiquitous in amorphous semiconductors and dielectrics. We link the MR and EDMR responses by measuring response amplitude for each technique versus bias. The observed EDMR and MR versus bias trends are nearly identical, suggesting that the defects responsible for each technique correspond to similar energy levels. Though circumstantial, our measurements provide strong evidence that the defects whose chemistry is plausibly identified via multiple frequency EDMR are primarily responsible for MR in the amorphous semiconductors and dielectrics in this study.
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<tr>
<td>κ</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>AOS</td>
<td>alkoxy silane</td>
</tr>
<tr>
<td>BEOL</td>
<td>back-end-of-line</td>
</tr>
<tr>
<td>CCL</td>
<td>copper-capping layer</td>
</tr>
<tr>
<td>CMOS</td>
<td>complementary metal-oxide-semiconductor</td>
</tr>
<tr>
<td>EDMR</td>
<td>electrically detected magnetic resonance</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>IC</td>
<td>integrated circuit</td>
</tr>
<tr>
<td>ID</td>
<td>impact damage</td>
</tr>
<tr>
<td>ILD</td>
<td>interlayer dielectric</td>
</tr>
<tr>
<td>LW</td>
<td>line width</td>
</tr>
<tr>
<td>MIS</td>
<td>metal-insulator-semiconductor</td>
</tr>
<tr>
<td>MOS</td>
<td>metal-oxide-silicon</td>
</tr>
<tr>
<td>MOSFET</td>
<td>metal-oxide-semiconductor field-effect transistor</td>
</tr>
<tr>
<td>MR</td>
<td>magnetoresistance</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OS</td>
<td>organosilane</td>
</tr>
<tr>
<td>REELS</td>
<td>reflection electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>RHP</td>
<td>remote hydrogen plasma</td>
</tr>
<tr>
<td>SDR</td>
<td>spin-dependent recombination</td>
</tr>
<tr>
<td>SDTAT</td>
<td>spin-dependent trap-assisted tunneling</td>
</tr>
<tr>
<td>SILC</td>
<td>stress-induced leakage current</td>
</tr>
<tr>
<td>TDDB</td>
<td>time-dependent dielectric breakdown</td>
</tr>
<tr>
<td>TTF</td>
<td>time-to-failure</td>
</tr>
<tr>
<td>VRH</td>
<td>variable range hopping</td>
</tr>
<tr>
<td>UVSE</td>
<td>ultraviolet spectroscopic ellipsometry</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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Chapter 1

INTRODUCTION

Since the invention of the transistor by Shockley, Bardeen, and Brattain,[1,2] the electronics industry has experienced incredible growth, resulting in billions of dollars of production and research, annually. The, so called, “Moore’s law,” has famously set the standard for transistor dimension scaling.[3] By scaling down transistor dimensions, the switching times of metal-oxide field-effect transistors (MOSFETs) are reduced, and overall integrated circuit (IC) performance is increased. However, the successful implementation of scaled MOSFETs into ICs requires careful consideration of several details. Common design considerations include, gate oxide thickness and dielectric constant, $\kappa$, MOSFET channel mobility,[5] interconnect resistivity, and interlayer dielectric (ILD) constant. The former have been circumvented, to some extent, via high-$\kappa$ dielectrics[4] strained silicon,[5] and copper interconnects.[6] However, the design and implementation of low-$\kappa$ ILDs, which physically separate interconnects, remains a problem for next generation ICs.[7] Reliability and performance of low-$\kappa$ dielectrics are primarily limited by electronic leakage and time-dependent dielectric breakdown (TDDB). In this work, non-conventional magnetic resonance techniques are utilized to better understand the nature of leakage currents and defects associated with the aforementioned reliability phenomena in low-$\kappa$ dielectrics.

Due to the inherent complexity of low-$\kappa$ dielectrics, conventional resonance measurements are often difficult to analyze, making defect identification or impossible. Thus, non-conventional magnetic resonance measurements are introduced as a method of
understanding defect chemistry and leakage in low-\(\kappa\) and other dielectric films. The techniques utilized in this study are conventional electron paramagnetic resonance (EPR) and an electrically detected analog of EPR in which the spin-dependent transport of electrically active electrons is detected. The technique is called electrically detected magnetic resonance (EDMR). Thus, an understanding of spin-transport is crucial to understanding the nature of defects in these systems via EDMR. As will be shown, performing EDMR measurements at high and low magnetic field sometimes allows for more definitive evidence regarding the chemical nature of defects involved in electronic transport in these systems. Additionally, performing EDMR at multiple metal-insulator-semiconductor (MIS) biases allows for a rudimentary understanding of defect energy levels.[8-10]

Additionally, we utilize EDMR measurements to understand near-zero magnetic field magnetoresistance (MR). MR phenomena have been reported in a variety of amorphous semiconductors and dielectrics, nearly all organics, but are not well understood.[9,11-14] In this work, MR phenomena are detected via spin-dependent trap-assisted tunneling (SDTAT) currents in amorphous dielectrics and semiconductors. By comparing MR and EDMR amplitudes as a function of MIS capacitor bias, we are able to provide strong evidence that defects detected via MR are of the same nature as those provisionally identified via multiple field/frequency EDMR.

1.1 Low-\(\kappa\) Interlayer Dielectrics for Modern Integrated Circuits

The leading material systems utilized for low-\(\kappa\) ILDs are PECVD films comprised of amorphous silicate networks doped with carbon (often referred to SiOC:H). The developmental approach to SiOC:H is to replace a fairly significant portion of the O-Si-3O
network with, for example, CH$_3$Si-3O in order reduce polarizability, thus reducing $\kappa$.[15-17] The implementation of dense (non-porous) SiOC:H (d-SiOC:H) dielectrics in state-of-the-art microprocessor technology was reported as early as 2004 for IBM’s 90 nm technology.[18] In order to further reduce the ILD constant, researchers began implementing porous SiOC:H (p-SiOC:H) as early as 2008. Several reliability issues including as electronic leakage, stress induced leakage current (SILC), and time dependent dielectric breakdown (TDBB) have since been reported in both d-SiOC:H and p-SiOC:H.[19-26]

It was recently suggested that the dominating paramagnetic defects in d- and p-SiOC:H films are various carbon dangling bonds.[27-30] Also reported are $E'$ centers (oxygen vacancies in SiO$_2$), hydrogen complexed $E'$ centers, various terminal organic groups, unidentified defects. Pomorski et al.[27] showed that the carbon dangling bond center defect densities are strongly correlated to electronic leakage, suggesting a potential role in other reliability issues such as TDBB. However, these conventional EPR studies have been somewhat inconclusive due to featureless spectra, and defect identifications were almost always tentatively assigned.[27,28-30] Reflection electron energy loss (REELS) measurements have revealed surface oxygen vacancies in both d- and p-SiOC:H films. In addition, defects states observed 2-6 eV above the valence band edge in p-SiOC:H are attributed to porogen residues. However, the chemical nature of the porogen residue defects is not well established. EPR measurements on p-SiOC:H films by Pomorski et al.[27] suggest that the porogen residue defects involve carbon dangling bond centers, but are inconclusive. Afanas’ev et al. have also reported carbon dangling bond-like spectra in p-SiOC:H films.[31] The EPR spectra are attributed to carbon ‘clusters’ by Afanas’ev et
al. by calculating (presumably zero-crossing) $g$ values of ranging from 2.0026–2.0032 via simulations.[31] However, the EPR studies provided by Afanas’ev et al. provide no evidence proving that observed spectra are not silicon dangling bond centers, or other defects.[31] Other groups have argued that the same carbon ‘clusters’ would have (presumably zero-crossing) $g$ values ranging from 2.0014-2.0024.[32,33]

The wide range of intrinsic low-$\kappa$ TDDB models in recent literature of dielectrics the lack of understanding of underlying physical phenomena. In the case of intrinsic low-$\kappa$ dielectric breakdown, that is, excluding effects of copper interconnects, the most widely considered time-to-failure (TTF) models are the E model,[20,21] the impact damage (ID) model,[22-24] and the 1/E model.[25,26] In the former, it is assumed that an external electric field stretch polar bonds, leading to bond weakening and breaking. As for the latter cases, it is assumed that charge injection may create or activate intrinsic defects. The underlying physical mechanism of the ID model is the breaking of hydrogen bonds. The ID model also utilizes Poole-Frenkel and Schottky emission as the primary conduction mechanisms responsible for breakdown. The 1/E was originally proposed for gate dielectrics, and suggests that high energy electrons cause impact ionization, which eventually leads to hole accumulation. This accumulation of holes creates a higher cathode field, increasing electron injection, and eventually leading to breakdown.[25,26] In long term studies,[34] the ID model seems to fit TTF data better than any other proposed models. However, this improved fit may be due to the use of an additional acceleration factor (adjustable parameter) not present in other proposed models.

Several groups have utilized bias and temperature stressing measurements in an attempt to study TDDB in d- and p-SiOC:H at the atomic scale. It has been found that
carbon-doping SiO$_2$ to lessen polarizability and create pores exacerbates TDDB.\cite{35,36}

The role of copper diffusion in TDDB is a widely debated subject. The strong electric field dependence of copper diffusion suggests that copper must be ionized prior to diffusing. For example, it was shown by Guo et al.\cite{37} that VUV irradiation may cause a reaction which generates charged hydroxyl and hydrogen atoms. If subjected to the appropriate bias, the hydroxyl ions may drift to the copper surface, ionizing the copper and allowing it to diffuse into the material. The breaking of hydrogen bonds is also considered in the ID model.\cite{22-24} It has recently been suggested that copper diffusion may not dramatically affect TTF, and that intrinsic breakdown mechanisms may dominate TDDB, even in porous low-κ dielectrics.\cite{38,39} This is typically attributed to the use of a dense low-κ transition layer which may also act as a diffusion barrier. Also, it has been shown that both TDDB and leakage become worse with increased porosity \cite{40}.

In Chapter 4, we utilize conventional EPR to attempt to understand defect chemistry in p-SiOC:H dielectrics as a function of fabrication steps. Since spectra are featureless, making defect identification difficult, we provide potential defect chemistries based on EPR studies in metalorganics and FTIR data when possible. The conclusions drawn from the conventional EPR studies are tentative. In the following sections, we provide stronger evidence regarding the nature of dangling bonds in these systems via multiple frequency EDMR. Finally, we investigate defect energy levels by comparing variable bias EDMR measurements with calculated band diagrams. The energy band gap and band offsets of these systems are measured using reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy (XPS), respectively. Understanding defect energy
levels enables a more detailed band diagram picture for future reliability studies of low-κ dielectrics.

1.2 Near-Zero Field Magnetoresistance (MR)

The dependence of a material’s electrical resistance upon an external magnetic field broadly constitutes magnetoresistance (MR). MR phenomena are most commonly reported in organic systems,[41-43] which are of great interest for spintronic materials due to relatively small nuclei, which result in fairly low spin-orbit coupling and long coherence times. However, there is still much debate as to whether spin-orbit coupling or hyperfine effects dominate spin-relaxation effects.[44,45] It is widely believed that MR observations in most organic and inorganic systems are due to spin transport phenomena through localized states within the systems under study. However, so-called ‘colossal’ MR in complex ferromagnetic oxides[46,47] has been attributed to polaron transport, which is fundamentally different than SDTAT. Spin-polaron mechanisms have also been reported in some organic systems in which MR phenomena are >10%.[42,48] This section outlines theoretical descriptions of MR phenomena due to SDTAT phenomena which are of use for understanding MR spectra observed in the inorganic semiconductors and dielectrics in this work. It is widely believed that MR spectra primarily reflect hyperfine interactions, rate of spin transport, and spin-relaxation mechanisms.[12,44,48,49] However, an exact relationship between MR spectra and underlying physical mechanisms has yet to be established. Thus, studying MR phenomena in a variety of systems via EDMR may be a valuable asset for developing spin-based quantum computation technologies.
1.2 References


Chapter 2

ELECTRON PARAMAGNETIC RESONANCE

2.1 Elementary Principals of EPR in Amorphous Semiconductors and Dielectrics

Electron paramagnetic resonance (EPR) EPR is a powerful analytical tool which allows for the identification and characterization of numerous defects in semiconductors and insulators. For the study of amorphous dielectrics and semiconductors provided in this work, the EPR response is primarily dominated by two phenomena: spin-orbit coupling, and electron-nuclear hyperfine interactions. The spin Hamiltonian for such a case is as follows:[1]

\[ \mathcal{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \sum_i \vec{I}_i \cdot \vec{A}_i \cdot \vec{S} \]  

(2.1)

Here, \( \mu_B \) is the Bohr magneton, \( \vec{B} \) is the applied magnetic field vector, \( \vec{S} \) is electronic spin operator, and \( \vec{I}_i \) is the nuclear spin operator for the \( i^{th} \) nucleus. \( \vec{g} \) and \( \vec{A}_i \) describe a defect’s surroundings, and are simply referred to as the \( g \) and \( A \) tensors. As will be discussed in more detail, the \( g \) tensor components are determined by spin-orbit coupling. \( A \) provides a measure of electron-nuclear hyperfine interactions. In the disordered, high hydrogen content dielectrics in this study, hyperfine interactions are mostly unresolved and the effects of \( g \) are averaged over all orientations.

In conventional EPR, a sample is placed in a high quality microwave cavity. The resonance response is typically detected via EPR induced changes in the microwave cavity quality factor. This measurement approach yields a maximum sensitivity of roughly \( 10^{10} \) paramagnetic defects. EPR is, in principle, sensitive to any paramagnetic defect in the
sample, including those which may not contribute to transport. Since conventional EPR is based upon magnetization of the paramagnetic electrons,[1] the conventional EPR response is very weak at low fields (and frequencies). As will be discussed in the following Chapter, electrically detected magnetic resonance (EDMR) offers much higher sensitivity and a nearly field and frequency independent sensitivity.

In the simplest case, excluding hyperfine interactions and taking the $g$ tensor components to consist of an (isotropic) constant, the Hamiltonian of expression (2.1) leads to a resonance condition may be written as

$$E = h\nu = g\mu_B B_{ext}. \quad (2.2)$$

Here, $h$ is Planck’s constant and $\nu$ is the frequency of an oscillating magnetic field, and $E$ is the energy splitting of the paramagnetic electron which is subjected to the external magnetic field, $B_{ext}$. This energy level splitting is referred to as the Zeeman splitting. A schematic of the Zeeman splitting of a free electron in an external magnetic field is shown in Fig. 2.1.

For a free electron, $g_e \cong 2.00232$. In real systems, $g$ is an orientation dependent factor which is typically expressed as a second rank tensor. As will be shown, the EPR line width due to $g$ tensor components is a function of the measurement field and frequency in (2.2). Hyperfine interactions, to zero order, are independent of the field and frequency of measurement.[1,2] Thus, comparisons of EPR spectra at multiple frequencies allow for distinctions to be made between broadening mechanisms. The broadening due to the distribution of $g$ tensor components is proportional to the field and frequency at which resonance occurs. Such a circumstance is schematically illustrated in Fig. 2.2 for the particularly simple case of an axially symmetric defect in which nearly all of the line width is due to $g$.[1,2] The $g$ dominated line shape has a well understood ‘powder pattern’ line
shape and a width corresponding to the range of \( g \) values. This is simply the result of a range of \( g \) values replacing the isotropic \( g \) value in expression (2.2). In this case, the low-field cut off response is at[1]

\[
B_\parallel \approx \frac{\hbar}{g_\parallel \mu_B}
\]  
(2.3)

and the high-field cut off is

\[
B_\perp \approx \frac{\hbar}{g_\perp \mu_B}.
\]  
(2.4)

(Since more defects will have a symmetry axis perpendicular to the quasi-static magnetic field than parallel to it, the absorption is weak at \( B_\parallel \) and strong at \( B_\perp \).[1])

From Fig. 2, (2.3), and (4) we see that

\[
\Delta B = B_\perp - B_\parallel \approx \frac{\hbar}{\mu_B} \left| \frac{g_\parallel - g_\perp}{g_\perp g_\parallel} \right| \nu
\]  
(2.5)

Since \( g_\parallel \approx g_\perp \approx 2 \) for silicon and carbon dangling bonds, we take \( g_\perp \times g_\parallel \approx 4 \), and (2.5) may be rewritten to express the range of \( g \) tensor components, \( \Delta g \), and \( g \) tensor dominated line width, \( \Delta B \), as follows:[1]

\[
\Delta g = g_\parallel - g_\perp \approx \frac{4\mu_B}{\hbar \nu} \Delta B
\]  
(2.6a)

\[
\Delta B \approx \frac{\hbar \nu}{4\mu_B} \Delta g
\]  
(2.6b)

Note that the \( g \) tensor dominated line width, as shown in (2.6b), is proportional to the measurement frequency, \( \nu \). For the simple case in which a powder pattern is present, one might directly determine the \( g \)-components, \( g_\parallel \) and \( g_\perp \), from the spectrum. However, if the
spectrum is broadened by disorder and unresolved hyperfine interactions, one should be still able to get a rough measure of the range of the $g$ tensor components directly by measuring spectra line widths at two very different frequencies and using (2.6a). This frequency dependent $g$ based line broadening provides us with a means of obtaining some physical and chemical information from featureless EDMR spectra of complex, amorphous dielectrics. As previously mentioned, the values and distribution of $g$ tensor components depend upon spin-orbit coupling. Though the $\Delta g$ broadening mechanism measured is associated with spin-orbit coupling, relating $\Delta g$ to defect structure and chemistry is not entirely straightforward. For example, using perturbation theory, we may calculate the approximate values for the $g$ tensor for the simple case of dangling bond defects as follows:[3]

$$g_{ij} = g_e + \Delta g_{ij}. \tag{2.7}$$

In (2.7),

$$\Delta g_{ij} = -2\lambda \times \sum_{n \neq 0} \frac{\langle 0|L_i|n \rangle \langle n|L_j|0 \rangle}{E_n - E_0}. \tag{2.8}$$

In (2.7) and (2.8), $g_e$ is the free electron $g$, $\Delta g_{ij}$ is the deviation in the $g$ tensor from $g_e$, $\lambda$ is the spin-orbit coupling constant, and $i$ and $j$ are the principle axes. $\lambda$ depends upon the charge within the nucleus and the electron wavefunction.[1,3,4] The numerator terms in the sum on the right hand side of (2.8) take into account the orbital angular momentum of the electron in state $n$, but the denominator terms take into account energy level differences with respect to the observed paramagnetic state energy. Unfortunately, we do not have the $E_n - E_0$ values. So, all things being equal, we might argue that, for example, a carbon dangling bond defect would have a smaller range of $\Delta g$ than a silicon dangling bond. However, in
reality, this may not be the case, as all things may not be equal. Significantly different $\Delta g$ ranges can occur for silicon bonds. For example, the E’ center, which exhibits a $\Delta g$ of about 0.0014,[5] is a silicon dangling bond back-bonded to three oxygen atoms. A silicon dangling bond back-bonded to three silicon atoms in amorphous silicon exhibits a $\Delta g$ of about 0.0055.[6] The reason that the E’ center has a relatively small $\Delta g$ compared to other silicon dangling bond centers is because the denominator terms of (8) are relatively large. Therefore, although there is a link between $\Delta g$ and nuclear charge and the size of nuclei involved in the measured site, a simple correspondence between a small $\Delta g$ and a small nuclear charge cannot be viewed as absolutely convincing. However, all things being equal, we would expect $\Delta g$ to be smaller for a carbon dangling bond than a silicon dangling bond spectrum; a large $\Delta g$ is very likely associated with an unpaired electron on a silicon, but the converse small $\Delta g$ assignment of a carbon dangling bond is more tentative.
Figure 2.1. Schematic of the Zeeman splitting of free electrons in an external magnetic field.

\[ E = g\mu_B B_{\text{ext}} \]
Figure 2.2. Simulated EPR spectrum of an axially symmetric dangling bond defect; the ‘powder pattern.’ Spectra are simulated using EasySpin.[2]
2.2 Experimental Method of Solid State EPR

As mentioned in the previous section, conventional EPR measurements are typically performed by placing a sample in a microwave cavity, and slowly varying the external magnetic field. A simplified schematic of an EPR spectrometer is shown in Fig. 2.3. Magnetic field modulation is applied parallel to the external magnetic field. The EPR response is then encrypted into the reflected microwave power at the modulation frequency. The reflected microwave power is altered at and near the EPR condition in (2.2) due to changes in the microwave cavity quality factor, as illustrated in Fig. 2.4(a). A lock-in amplifier is utilized to convert the AC response to a DC voltage, which is converted from an analog signal to a digital file using computer software. The analog-digital conversion software used in this work is LabVIEW. The observed EPR response is the derivative of an absorption spectrum, as shown in the simulation in Fig. 2.4(b).

Defect concentration may be measured via conventional EPR by comparing spectra amplitudes of a reference sample with a known defect concentration, and the subject sample in question. The reference sample is shown in Fig. 2.3. In this schematic, a TE_{104} cavity is utilized. The TE_{104} cavity allows for a reference sample and subject sample to be placed in a tuned cavity simultaneously. To make an EPR measurement in a given sample, the sample modulation coils are activated to provide the sample spectrum. Then, the spin standard coils are activated to provide a spectrum of the reference sample. If both measurements are made with the microwave power low enough so that the spin systems are in equilibrium, the defect concentration of the subject sample is equal to the defect concentration of the reference sample multiplied
by the ratio of the integrated intensities of the reference sample and subject sample EPR spectra, respectively. This method of measuring defect concentration is typically only accurate to about ±10% in absolute number, but is still quite useful for measuring fairly large changes in defect concentration due to fabrication process, temperature stresses, and etc.

Another useful measurement technique utilized in EPR practice is fast-passage EPR.[7-9] In fast-passage EPR, the EPR signal is detected at twice the modulation frequency. Fast-passage detection can sometimes be useful for ‘sharpening’ EPR spectra, thus allowing for the detection of hyperfine or $g$ related structure in some cases. This sharpening is a result of differences in spin-relaxation times of specific defects which can, to some extent, be optimized by adjusting modulation frequency and amplitude, and microwave field amplitude. It has been shown that, for systems with long spin-lattice relaxation times, EPR spectra detected at higher order harmonics may be observed as absorption spectra.[7] Since defects with shorter spin-lattice relaxation times do not meet the criteria for fast-passage effects, they are not observed at at higher order harmonics. Thus, fast-passage EPR may be useful for extracting defects with fairly long spin-lattice relaxations times, while not detecting those with shorter spin-lattice relaxation times. Since fewer defect chemistries are observed via fast-passage EPR, observed spectra are often sharper, and sometimes reveal additional features which may be useful for defect identification.
Figure 2.3. Schematic representation of an EPR spectrometer.
Figure 2.4. (a) Microwave absorbance as a function of applied magnetic field. (b) Measured EPR amplitude as a function of magnetic field.
2.3 References


Chapter 3

SPIN DEPENDENT TRANSPORT AND ITS ELECTRICAL DETECTION

3.1 Introduction: Spin Dependent Trap Assisted Tunneling (SDTAT)

Spin dependent transport phenomena have been of interest since the first observations of spin dependent recombination (SDR) via electrical detection by Lepine in 1972.[1] SDR was later theoretically explained by Kaplan et al.[2] and has since been observed in a wide variety of semiconductors and semiconductor/dielectric interfaces.[3-6] SDR, which can be electrically detected as will be explained in the following section, has been used as a diagnostic tool for electrically active point defects in a variety of electronic materials.[5-8] In addition, since the introduction of the concept of quantum information processing, spin-transport phenomena have also drawn interest for quantum computation applications.[9-11] In this work, spin-dependent trap assisted tunneling (SDTAT) is the primary detected spin-transport phenomenon. SDTAT has been previously reported,[12-16] but is far less commonly reported than SDR.

At an elementary level, SDTAT may be understood by considering two coupled paramagnetic defect centers in a dielectric material, as illustrated in Fig. 3.1. (Note that this process occurs in other systems, including semiconductors.[16,17]) As shown in Fig. 3.1, the electron pair may be in two spin state formations; that is, triplet formation and singlet formation. When the spins are aligned, the pair formation is termed a triplet state, illustrated in Fig. 3.1(a), and the tunneling process is not allowed due to the Pauli exclusion principle. However, if the two electrons are in a singlet state, as is illustrated in Fig. 3.1(b), the tunneling process will be allowed. As will be shown, the ratio singlet/triplet states may be altered via external magnetic fields, and SDTAT may be detected electrically.
Fig. 3.1. Schematic illustration of SDTAT. (a) the electron spins are aligned, and the spin pair is in triplet formation. In a triplet state, the tunneling process is not allowed. (b) the two electron spins are in opposite directions, and the spin pair is in a singlet state. In a singlet state, the tunneling process is allowed.
Thus, with an external magnetic field applied, the electron spin quantization axis will be the vector sum of the local hyperfine and external magnetic fields. These local hyperfine fields are important to consider when analyzing SDTAT phenomena. For SDTAT events measured via EDMR, hyperfine interactions should follow (2.1), as will be explained in the following section. However, for the case of near-zero magnetoresistance (MR), the role of hyperfine interactions upon spectra line widths is not well understood.

Another consideration worth noting is the number of tunneling centers which may be involved in the SDTAT process. In thin films, we expect tunneling to occur through one or two tunneling centers. An example of such a case will be described in Chapter 5 in 3 nm silicon nitride. However, in fairly thick films, (> 10 nm), we expect that tunneling will occur through several defects. This process is referred to as variable range hopping (VRH).[18,19] Spin dependent VRH has been reported in amorphous semiconductors and dielectrics.[16,20] As will be demonstrated, the process follows the temperature dependence set forth by Mott for transport in amorphous semiconductors.[18,19]

3.2 Electrically Detected Magnetic Resonance (EDMR) via SDTAT

SDTAT via EDMR was first reported in SiO$_2$ by Stathis in 1989.[21] Variable bias SDTAT/EDMR measurements were later performed by Ryan et al. to calculate defect energy levels in silicon oxynitride.[13] More recently, spin dependent VRH has been detected via EDMR in amorphous semiconductors[16] and dielectrics.[20] The power and utility of EDMR via both SDTAT and SDR for the study of electronic materials are a result of the electrical detection of EPR. In the previous Chapter, we acknowledged the analytical power of EPR, which can detect and identify paramagnetic defect centers at the atomic scale. However, EPR has several limitations; almost all of which may be
circumvented via EDMR. First, EPR detects all paramagnetic defect centers. Conversely, EDMR only detects defects which are related to electronic transport mechanisms. Additionally, the sensitivity of EDMR is about 6 orders of magnitude better than EPR, allowing defects to be detected in nano-scale electronics materials, and fully processed devices. Finally, the sensitivity of EDMR is nearly independent of the field and frequency of measurement. Thus, unlike EPR, measurements can be performed at very low magnetic fields and frequencies without loss of sensitivity.

EDMR occurs due to singlet/triplet state transformation via EPR. As discussed in the previous section, the tunneling process in Fig. 3.1 is allowed if electrons are arranged in a singlet state, but not if they are arranged in a triplet state. If the system is in a large magnetic field, both electrons will tend to align with external magnetic field. However, by applying an oscillating magnetic field of frequency $\nu$ to satisfy the EPR condition in 2.1, one or more of the spins may ‘flip,’ resulting in a triplet-singlet transformation. The change in the singlet/triplet ratio results in a net change in tunneling current, which may be detected electrically.[2,12-16] Thus, defects detected via SDTAT/EDMR are directly related to trap-assisted tunneling. Since the SDTAT process is not a strong function of magnetization, measurements may be performed at low fields and frequencies without loss of sensitivity, as previously mentioned. This allows for a rough calculation of $g$ tensor components via (2.6a) from the previous Chapter. Additionally, measurement apparatus are much cheaper than those used for conventional EPR. There is currently no theoretical limit to sensitivity for SDTAT, which has been detected in quantum dots with two electron spin states.[22] In this work, SDTAT is detected via EDMR in 3 nm a-SiN:H, which presumably occurs predominantly through a single defect within the a-SiN:H film.
3.3 Near-Zero Field Magnetoresistance (MR) via SDTAT

As described in Chapter 2, magnetic resonance has long been used to understand interactions between electron spins and their surroundings. MR phenomena via SDTAT or VRH, which have more recently been demonstrated,[14,20,22,23] also show great potential for understanding spin-transport phenomena. Unfortunately, the effect of quantum effects such as local hyperfine fields, spin-orbit coupling, dipolar interactions, and exchange interactions upon electron spins and resulting MR spectra are poorly understood.

Near-zero field MR phenomena are believed to be a result of mixing between singlet and triplet states at and near zero magnetic field.[22,23,32] This can be explained by the reorientation of the electron spin quantization axis as the external magnetic field approaches zero. At fairly large magnetic fields (≈ 100 G), as previously mentioned, the electron spin quantization axis will be the vector sum of the external magnetic field and local magnetic field, as shown in Fig. 3.2(a). As the magnetic field is slowly decreased toward zero-field, the electrons will tend to the local hyperfine field, as shown in Fig. 3.2(b). This reorientation of spins changes the singlet/triplet ratio, thus changing the tunneling current. Similarly to EDMR, this change in current can be detected electrically. It should be noted that, though both EDMR and MR may be detected electrically, the underlying physical mechanism for each respective technique is fundamentally different. For EDMR, singlet/triplet transformation via EPR results in a detectable change current, while MR phenomena occur due to mixing of singlet and triplet states as the external magnetic field approaches zero. As mentioned in the previous section, the nature of EDMR spectra are fairly well understood due to the breadth of knowledge of EPR. However, the
nature of MR spectra is not well understood, and a complete connection between hyperfine interactions, spin-orbit coupling, and other quantum effects with MR spectra is still unavailable.

It can easily be shown via the spin Hamiltonian (refer to the one-electron spin Hamiltonian in Chapter 2, Expression 2.1) that the Zeeman splitting at exactly zero magnetic field is zero. However, the effect of spin-orbit coupling on MR spectra is not trivial. It is fairly well understood that for defects with relatively large breadths of $g$ tensor components, $\Delta g$, spins decohere faster than those with smaller $\Delta g$ values. In other words, spin-orbit coupling effects decrease spin lifetime.[34,35] A theoretical description of SDTAT in materials with large spin-orbit coupling has been provided by Harmon and Flatte.[27] In their analysis, it is shown that electrons become depolarized as they hop from site to site due to large $\Delta g$. Thus, the picture in Fig. 3.2(a) may become skewed as electrons hop from site-to-site. Since we can provide a measure of $\Delta g$ via multiple frequency EDMR measurements, a comparison of $\Delta g$ to MR spectra may be of use for understanding the impact (or lack thereof) of spin-orbit coupling upon MR spectra.

It is widely believed that most of the zero-field MR spectra line widths are due to hyperfine interactions.[23,32] Such a belief is justified by the reorientation of the electron spin toward the local hyperfine field near zero magnetic field. Distinct hyperfine splittings have been detected via SDR/MR in 4H-SiC MOSFETs,[23] and n-GaAs heterostructures.[34] It was shown in the 4H-SiC study that these hyperfine interactions may be used to identify the nature of the defects in 4H-SiC systems via comparisons with EDMR spectra.[23] However, distinct hyperfine interactions have yet to be reported via
SDTAT/MR in amorphous systems. This is likely due to both the inherent disorder of amorphous systems, and the lack of available SDTAT/MR studies in amorphous systems.

In this work, we will utilize comparisons between EDMR and MR measurements to gain insight into the underlying phenomena responsible for MR. Multiple frequency EDMR will be used to understand defect chemistry in disordered systems. By comparing EDMR and MR amplitudes as a function of capacitor bias, we will link defects identified via EDMR to MR phenomena via defect energy levels.
Figure 3.2. Simplified schematic representation of an electron quantization axis at (a) an arbitrary external magnetic field, $B_{\text{ext}} = B_0$ (on the order of 100 Gauss), (b) an arbitrary magnetic field less than $B_0$, and (c) zero external magnetic field. The green arrow represents the quantization axis of the electron spin, $B_{e-}$, and the local field experienced by the electron due to its surroundings is $B_{\text{local}}$. 
3.4 References


Chapter 4

MAGNETIC RESONANCE STUDIES OF LOW-κ DIELECTRICS

4.1. EPR Study of p-SiOC:H Dielectrics as a Function of Fabrication Steps

Films investigated in this section were deposited on 300 mm diameter Si (001) wafers with a native oxide via plasma enhanced chemical vapor deposition (PECVD) using either organosilane (OS) or alkoxysilane (AOS) precursors in combination with diluent gases such as He, H$_2$, CO$_2$, N$_2$ and NH$_3$.[22,24] The AOS films were deposited at lower temperatures ranging from 200 to 275°C in order to incorporate a second phase organic pore building “porogen.” The porogen was removed from the latter films to create increased porosity via a variety of methods including combined UV and 400°C thermal curing and/or a 250°C RHP.[37] (Table 4.1 summarizes the precursors, post-deposition processes, κ-values, porosity, and composition for powders investigated in this study.)

Since signal-to-noise constrains remain a problem for EPR studies of low-κ thin films, we utilize a-SiOC:H powders, which provide a large volume of a-SiOC:H, to circumvent this problem. To obtain the powders, the films were mechanically separated from the substrates. EPR measurements were performed at room temperature on an X-band Bruker EMX spectrometer with a TE$_{102}$ cavity. An NMR Gaussmeter was used to accurately measure the magnetic field.

OS a-SiOC:H powders, which were grown without the introduction of sacrificial porogens, were studied pre- and post-UV curing. (Post-UV cure, κ=2.3.) Fig. 4.1 illustrates a pre-UV cure EPR spectrum. The spectrum is dominated by a 5.5 Gauss wide line with a zero-crossing $g$ of 2.0027, as shown in Fig. 4.1. (Table 4.2 summarizes EPR results in this paper.) The measured defect concentration is $3\times10^{15}$ cm$^3$. The narrow line width and zero-
crossing $g$ close to that of the free electron $g (= 2.00232 \ldots)$ likely indicate that the spectrum is primarily due to carbon dangling bonds.[22,23,27] An additional much weaker two line spectrum is also present, with two lines separated by about 16.5 Gauss. The presence of two lines indicate that the defect is coupled to a hydrogen atom. Similar spectra have been observed in non-porous films.[22] Since there is no porogen within the OS a-SiOC:H powder, the EPR response of Fig. 4.1 must be due to dangling bonds within the a-SiOC:H bulk. The presence of hyperfine interactions separated by roughly 16.5 Gauss indicates the presence of nearby hydrogen. Pomorski et al.[22] have observed a 16.5 Gauss splitting, which was tentatively attributed to defect coupling with either a SiH$_3$ or a CH$_3$ molecule. The presence of CH$_x$ groups and absence of SiH$_3$ groups in the OS precursor used in this study[38] likely indicate that the hyperfine interactions observed in Fig. 4.1 are due to CH$_x$ groups. If the observed hyperfine interactions were due to CH$_3$, a 1:3:3:1 pattern would be present.[39] The hyperfine splitting of 16.5 Gauss could be due to a CH$_3$ beta (next nearest) carbon,[40] which should have additional hyperfine side peaks at about 5.5 Gauss. If this were the case, the 5.5 Gauss side peaks would be buried in the center line of the spectrum in Fig. 4.1.

However, given the OS precursor, one plausible arrangement for a carbon dangling bond back-bonded to one methyl group, as shown in Fig. 4.2, option 1. This arrangement would have additional hyperfine splitting due to the alpha carbon, and would result in a far more complicated spectrum than observed in Fig. 4.1.[41]
Table 4.1. Summary of precursors, κ-values, porosity, and composition post curing.

<table>
<thead>
<tr>
<th>a-SiOC:H Precursor</th>
<th>Post-Deposition Treatments</th>
<th>Porogen</th>
<th>κ</th>
<th>% Porosity</th>
<th>% Si</th>
<th>% O</th>
<th>% C</th>
<th>% H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(C$_x$H$_y$)$_4$</td>
<td>UV</td>
<td>No</td>
<td>2.55</td>
<td>15</td>
<td>12.0</td>
<td>15.7</td>
<td>22.8</td>
<td>49.6</td>
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<tr>
<td>AOS</td>
<td>UV</td>
<td>Yes</td>
<td>2.3</td>
<td>33.5</td>
<td>15.2</td>
<td>25.4</td>
<td>23.1</td>
<td>37.4</td>
</tr>
<tr>
<td>AOS</td>
<td>RHP+UV</td>
<td>Yes</td>
<td>2.0</td>
<td>45</td>
<td>12.8</td>
<td>25.8</td>
<td>23.8</td>
<td>38.6</td>
</tr>
</tbody>
</table>
Table 4.2. Summary of EPR results in powders utilized in this studied organized by post-deposition processes. (C_{db} = carbon dangling bond, Si_{db} = silicon dangling bond, and PR = porogen related.)

<table>
<thead>
<tr>
<th>a-SiOC:H Precursor</th>
<th>Post-Deposition Treatments Received</th>
<th>Zero-crossing g</th>
<th>Line width (Gauss)</th>
<th>Defect Concentration (cm^3)</th>
<th>Primary Defect Assignment</th>
<th>Defects Present at Lower Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS</td>
<td>None</td>
<td>2.0027</td>
<td>5.5</td>
<td>3x10^{15}</td>
<td>C_{db} (bulk)</td>
<td>N/A</td>
</tr>
<tr>
<td>OS</td>
<td>UV</td>
<td>2.0032</td>
<td>7</td>
<td>2.3x10^{17}</td>
<td>Si_{db} (bulk)</td>
<td>C_{db} (bulk)</td>
</tr>
<tr>
<td>AOS</td>
<td>None</td>
<td>2.0031</td>
<td>9</td>
<td>2.1x10^{17}</td>
<td>X_{db} (PR)</td>
<td>C_{db2} (bulk)^a</td>
</tr>
<tr>
<td>AOS</td>
<td>UV</td>
<td>2.0030</td>
<td>7</td>
<td>2.2x10^{17}</td>
<td>X_{db} (PR)</td>
<td>CH_{3}</td>
</tr>
<tr>
<td>AOS</td>
<td>RHP</td>
<td>2.0026</td>
<td>1.5</td>
<td>2x10^{15}</td>
<td>C_{db2} (bulk)</td>
<td>N/A</td>
</tr>
<tr>
<td>AOS</td>
<td>RHP + UV</td>
<td>2.0028</td>
<td>11</td>
<td>5.9x10^{17}</td>
<td>Defect A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

^aHere, the defect concentration of the C_{db2} bulk defect is 2x10^{15}. Note that the defect assignments, Si_{db} and C_{db} are quite tentative at this time.
Figure 4.1. EPR spectrum of an OS a-SiOC:H powder prior to UV curing. Arrows indicate hyperfine interactions. The peak-to-peak line width is 5.5 Gauss.
It is also possible that the defect is a carbon dangling bond is back-bonded to a CH₂, which would lead to a hyperfine splitting roughly 17.7 Gauss.[41] The OS precursor used in this film contains H₂C=CH-Si networks.[24] If a hydrogen atom was removed from the CH group, the corresponding defect would resemble option 2 in Fig. 4.2. Similar defects have a zero-crossing g of 2.0027 and a hyperfine splitting due to the beta CH₂ of 17.7 Gauss.[41] A variety of silicon dangling bonds could also plausibly exhibit a zero-crossing g of 2.0027. The OS precursor predominantly consists of organosilyl (Si-(CH₃)₃) groups.[38] Thus, dangling bonds of the form (CH₃)₃-xSiHₓ, where the dot represents a dangling bond and x is 0, 1, or 2, are possible. Fig. 4.2 option 3 schematically illustrates an organosilyl radical with x = 1. Of the three organosilyl radicals, the x = 1 configuration is the only plausible arrangement since the hyperfine coupling constant for the hydrogen atom bonded to the central silicon would be 16.99 Gauss.[42] (The x = 0 and x = 2 arrangements would exhibit significantly different patterns.)[42] However, if the defect responsible for the spectrum in Fig. 4.1 was the (CH₃)₂SiH radical, additional hyperfine lines due to the (CH₃)₂ groups would be observed at separations of approximately 31 and 45 Gauss.[42] Thus, we rule out the possibility that Fig. 4.1 is a result of a dominating presence of organosilyl radicals. The OS films exhibit a 15.7% oxygen, which might suggest the presence of E’ centers (oxygen vacancies in SiO₂) and E’ variants, such as the Eδ’ and Eγ’ centers.[43-45] (For a discussion of these defects, see Refs. 43-45.) We rule out a dominating presence of E’ centers since the zero-crossing g of 2.0027 is not agreement with E’ center-like defects, and no ²⁹Si hyperfine interactions[43,45] are present in EPR measurements performed at high sensitivity over a wide range magnetic field in the OS a-
SiOC:H powder. Of the above listed options, option 2 in Fig. 4.2 seems to be the most reasonable defect assignment for the spectrum in Fig. 4.1.
Figure 4.2. Schematics of potential defects associated with the spectrum in Fig. 4.1.
Post UV treatment, EPR measurements on the OS a-SiOC:H powder, as shown in Fig. 4.3, reveal an increase in paramagnetic defect density of two orders of magnitude, to $2.3 \times 10^{17}$ cm$^{-3}$. EPR spectra with a zero-crossing $g$ of 2.0032 and line width of 7 Gauss, identical to the spectrum in Fig. 4.3, have previously been ascribed to carbon dangling bonds in both porogen- and non-porogen-derived a-SiOC:H films post-UV treatment.[3] It has also been argued that silicon dangling bonds may be formed from UV cures.[22,46-49]

The OS precursors used in this study contain unsaturated terminal organic groups, which could result in carbon dangling bond generation via UV treatment. It is also possible that silicon dangling bonds are generated either by damage of the Si-O-Si network, or by removal of hydrogen of Si-H bonds. Previous studies utilizing electrically detected EPR at multiple frequencies have provided strong evidence that silicon dangling bonds may be formed by UV treatments in porous a-SiOC:H systems.[46]

EPR measurements have also been performed on AOS a-SiOC:H powders as a function of post-deposition processing steps. Unlike the OS films, sacrificial porogens are introduced into the AOS-derived a-SiOC:H films. EPR measurements on the AOS a-SiOC:H powders were made prior to post-processing steps, post UV radiation only, post RHP only, and post successive RHP and UV treatments. (Post UV radiation only, the AOS a-SiOC:H powder in this study exhibits $\kappa = 2.3$. Post RHP and subsequent UV treatment, the AOS a-SiOC:H powder exhibits $\kappa = 2.0$.)

An EPR trace on the AOS a-SiOC:H powder prior to UV or RHP treatments is shown in Fig. 4.4. The zero-crossing $g$ (2.0031) and line width of 9 Gauss are similar to those associated with a spectrum linked to a defect termed carbon dangling bond 1 (Cdb1) in the earlier study of Pomorski et al.[3] The measured defect concentration is $2.1 \times 10^{17}$ cm$^{-3}$. 


3, a paramagnetic defect concentration two orders of magnitude greater than the as-processed OS a-SiOC:H material. However, unlike the Cdb1 spectrum reported by Pomorski et al.,[22] the spectrum in Fig. 4.4, although apparently dominated by one defect spectrum, also involves one or more additional overlapping spectra. To better understand the nature of defects responsible for Fig. 4.4, fast passage EPR measurements were performed on these samples. Since fast-passage measurements can sometimes ‘sharpen’ EPR spectra, they can sometimes provide additional insight when overlapping spectra are present.[50] The fast-passage EPR trace in Fig. 4.5 on the AOS a-SiOC:H powder pre-UV clearly reveals the presence of two distinct spectra. (Due to the nature of fast-passage detection, an absorption spectrum is observed,[50] in conventional EPR measurements, a derivative-like spectrum is observed. To make comparisons between the fast-passage and conventional EPR measurements more straightforward, the fast-passage trace in Fig. 4.5 is a derivative of the measured fast-passage spectrum.) The two distinct spectra appear to be identical in line width and zero-crossing g to the defects termed ‘Cdb1’ (line width = 7 Gauss, g = 2.0031) and ‘Cdb2’ (line width = 1 Gauss, g = 2.0026) observed by Pomorski et al.[22] For reasons explained later, we will refer to the 7 Gauss, g = 2.0031 defect as Xdb, merely to indicate that this defect may not be a carbon dangling bond. We deconvolute the two spectra by simulating each defect individually using EasySpin,[51] allowing for a rough calculation of relative defect concentrations. The measured fast passage spectrum versus simulation is shown in Fig. 4.5. The relative defect concentrations for Xdb and defect 1 are found to be $X_{Xdb} = 2 \times 10^{17} \text{ cm}^{-3}$, and $X_{Cdb2} = 2 \times 10^{15} \text{ cm}^{-3}$, respectively. Again, we observe a dominating presence of paramagnetic sites prior to UV or RHP treatments. However, as mentioned previously, the defect concentration of dangling bonds is two
orders of magnitude higher for the AOS a-SiOC:H powder than for the OS a-SiOC:H powder, indicating that the introduction of a

![EPR Spectrum](image)

Figure 4.3. EPR spectrum of the OS a-SiOC:H powder post UV curing. The peak-to-peak line width is 7 Gauss.
Figure 4.4. EPR spectrum of the AOS a-SiOC:H powder prior to RHP treatment or UV curing.
porogen results in a significant increase in defect concentration. $X_{\text{db}}$ has previously been linked to porogen.[22] The organic porogens in this study contain aromatic carbons terminated by hydrogen.[52]

If unresolved hyperfine interactions dominate the carbon dangling bond spectrum line width, it has been suggested that the number of fused rings can be predicted by the line width.[53] Given the number of rings of the precursors used in this study,[52] and the line width prediction by Kleber,[53] it is likely that other mechanisms result in the line width. Barklie et al.[40] have shown that EPR line widths of carbon dangling bonds in amorphous carbon with varying sp$^3$ content can be a combined function of hyperfine, dipolar, and exchange interactions. It is thus likely that there are multiple sources of the line width for the spectrum associated with $X_{\text{db}}$, making a prediction of local defect structure quite difficult.

$C_{\text{db2}}$ has been observed in dense films grown with an identical AOS precursor. Thus, it is very likely that $C_{\text{db2}}$ is a bulk defect. The zero-crossing $g$ and line width attributed to $C_{\text{db2}}$ could also be consistent with a silicon dangling bond. However, the strong Si-O-Si network in these films as indicated by FTIR measurements,[22] suggests that E’ centers would be the dominating silicon dangling bond center in these films. However, the spectrum attributed to $C_{\text{db2}}$ is dramatically different than E’ center spectra,[43-45] providing circumstantial evidence in favor of the narrow spectrum in Fig. 4.5 being due to carbon dangling bonds. (Though FTIR measurements cannot detect Si-Si bonds, we rule the presence of silicon dangling bonds back-bonded to one or more silicon atoms since
Figure 4.5. Measured (blue) and simulated (orange) EPR spectra in AOS a-SiOC:H prior to RHP treatment or UV curing.
such defects would have zero-crossing $g$ values of about 2.0055.[41] The narrow line width and lack of hyperfine interactions suggest that the carbon dangling bond is at least a few bond separations from any hydrogen atoms. FTIR spectra in the UV treated AOS film used in this study do not indicate a strong Si-C network, so we expect that the back-bonds of Cdb2 primarily consist of carbon and oxygen. It has been shown that (presumably zero-crossing $g$) of carbon dangling bonds in a-SiOC:H systems will vary only slightly with back-bond variation.[56] Some potential defect structures of Cdb2 are shown schematically in Fig. 4.6.

Post UV treatment only, we observe a spectrum, shown in Fig. 4.7, with a line width and zero-crossing $g$ in agreement with $X_{db}$, and a corresponding defect concentration of $2.2 \times 10^{17}$ cm$^{-3}$. This result is similar to above observations for the OS a-SiOC:H powder, except that the porogen related defect seems to be present prior to UV treatment in the AOS a-SiOC:H powder. This result is in agreement with previous suggestions that the UV cure leaves behind a porogen residue, resulting in a large defect concentration.[22,47,56] To better understand the nature of the porogen residue related defect, fast-passage EPR measurements are performed. Fast-passage EPR measurements are shown in Fig. 4.8. The narrow spectrum ascribed to Cdb2 is present, suggesting that the UV likely has little or no effect on the Cdb2 bulk defect, which was present prior to UV radiation at low ($2 \times 10^{15}$ cm$^{-3}$) concentration. A peak at 2.0005 is also present. This is consistent with an E’ center.[43] It is possible that the E’ centers were present prior to UV treatment, but the E’ response was obscured by the $X_{db}$ signature illustrated in Fig. 4.5. Another possibility is that the E’ centers were generated by UV radiation, as previous findings suggest.[46]
It has been suggested that RHPs are an effective means of removing porogens without damaging the a-SiOC:H bonding network.[35,56] To understand the effects of RHP treatments, we perform EPR on the AOS a-SiOC:H powder after RHP treatments with no additional UV cure. Post RHP, an EPR spectrum with a line width of about 1.5 Gauss and a zero-crossing $g$ of 2.0026 is observed, as shown in Fig. 4.8. This spectrum is virtually identical to the Cdb2 spectrum of Pomorski et al.[22] simulated in Fig. 4.3. We measure a defect concentration of $2 \times 10^{15}$ cm$^{-3}$. This, along with our EPR results in AOS a-SiOC:H powder, indicate that the RHP treatment removes the $X_{db}$ signature from the AOS a-SiOC:H while leaving the Cdb2 signature unchanged. This confirms previous suggestions that RHP cures are an effective means of removing porogens while not damaging the Si-O-Si network, and leaving terminal methyl groups intact.[38,56]

Post RHP treatment and subsequent UV curing, a broad spectrum, as shown in Fig. 4.9, (about 11 Gauss) with a zero-crossing $g = 2.0028$ is observed, and the corresponding defect concentration is $5.9 \times 10^{17}$ cm$^{-3}$. This spectrum was observed by Pomorski et al.,[3] and tentatively ascribed to a silicon dangling bond. Such an assignment seems reasonable based upon the line width. As previously mentioned, stronger evidence for the identity of this spectrum was recently provided and links the spectrum to silicon dangling bonds formed by damaging of the Si-O-Si network via UV treatment.[46] The increase in defect concentration after UV treatment in this AOS powder supports our previous findings:[46] that silicon dangling bonds are generated by UV treatment. Thus, it is likely that the UV
Figure 4.6. Schematics of potential defect structures of $C_{db2}$. See text for further explanation.
treatments damage the Si-O-Si network, or break Si-H bonds, resulting in an increase in silicon dangling bonds.

In conclusion, both porogen (AOS precursor) and non-porogen (OS precursor) derived porous a-SiOC:H systems, we observe carbon dangling bonds at fairly low concentrations ($\sim 10^{15}$) prior to UV or RHP treatments, which we attribute to paramagnetic centers within the a-SiOC:H network. However, the introduction of sacrificial porogens to the a-SiOC:H network introduces a two order of magnitude increase in defect concentration. For the non-porogen derived a-SiOC:H films, the UV treatment introduced a two order of magnitude increase of tentatively ascribed carbon dangling bonds, indicating that the UV treatment damages the a-SiOC:H network. After UV treatment, the defect concentration of the porogen derived a-SiOC:H remains virtually the same. This result links the defects which were present post-deposition to the porogen, and suggests that the UV treatment does not fully remove the porogen. The introduction of the RHP treatment reduces the defect concentration of the AOS a-SiOC:H system by two orders of magnitude. This dramatic decrease in defect concentration indicates that the RHP treatment effectively removes the porogen-related defect. Finally, successive RHP and UV treatments introduce defects which we attribute to silicon dangling bonds.
Figure 4.7. EPR spectrum of the AOS a-SiOC:H powder post UV treatment. The peak-to-peak line width is 7 Gauss.
Figure 4.8. EPR spectrum of the AOS a-SiOC:H powder after RHP treatment. The peak-to-peak line width is 1.5 Gauss.
Figure 4.9. EPR spectrum of the AOS a-SiOC:H powder post successive RHP + UV treatments. The peak-to-peak line width is 11 Gauss.
4.2 EDMR Study of d-SiOC:H and a-SiCN:H Dielectrics

All films investigated in sections 4.2 and 4.3 were deposited on 300 mm diameter Si (001) wafers with a native oxide via plasma enhanced chemical vapor deposition using various silane, organosilane, alkoxy silane, and organic precursors in combination with diluent gases such as He, H₂, CO₂, N₂ and NH₃.[22-25,58,59] The non-porous films were deposited at temperatures on the order of 400°C while the porous films were deposited at lower temperatures ranging from 200 to 275°C in order to incorporate a second phase organic pore building “porogen.” The porogen was removed from the latter films to create increased porosity via UV treatment and 400°C thermal curing.[37] Table 4.3 summarizes the precursors, κ-values, thicknesses, and compositions of the low-κ films in this section.

EDMR measurements in this section were made on several commercial and home-built spectrometers. X-band EDMR measurements were made on a homemade EDMR spectrometer which includes a 4 inch Lakeshore electromagnet with a Micro-Now X-band microwave bridge and TE₁₀₂ cavity. In order to accurately measure zero-crossing g values, we utilize an NMR Gaussmeter. Low-field EDMR measurements were performed on home-built EDMR spectrometers. In the low-frequency EDMR measurements, an RF frequency magnetic field is supplied by a Stanford Research Systems signal generator and a Doty Scientific RF coil and tuning circuit. The magnetic fields utilized in the low-field measurements were generated by a homemade set of nested Helmholtz coils. EDMR measurements were performed on Al/Ti/dielectric/p-Si capacitors utilizing dielectric fields of approximately -2 MV/cm. In dense films, EDMR measurements were performed at room temperature. For porous films, EDMR measurements were made at elevated temperatures of about 400 K.
To demonstrate the potential utility of the concepts described above, we compare EDMR line widths in a-Si:H and a-C:H films. (We know we have unpaired electrons on silicon in a-Si:H)

Table 4.3. Summary of precursors, $\kappa$-values, thicknesses, and composition (provided for low-$\kappa$ systems) for films studied via EDMR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>$\kappa$</th>
<th>Thickness (nm)</th>
<th>%Si</th>
<th>%O</th>
<th>%C</th>
<th>%N</th>
<th>%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H</td>
<td>NA</td>
<td>NA</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a-C:H</td>
<td>NA</td>
<td>NA</td>
<td>500.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d-SiOC:H #1</td>
<td>OS#2</td>
<td>5.8</td>
<td>7.0</td>
<td>20.4</td>
<td>19.6</td>
<td>22.6</td>
<td>0.0</td>
<td>32.5</td>
</tr>
<tr>
<td>d-SiOC:H #2</td>
<td>OS#2</td>
<td>3.2</td>
<td>8.0</td>
<td>20.3</td>
<td>34.0</td>
<td>15.5</td>
<td>0.0</td>
<td>30.2</td>
</tr>
<tr>
<td>p-SiOC:H #1</td>
<td>AOS#1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-SiOC:H #1*</td>
<td>AOS#1</td>
<td>2.3</td>
<td>17.0</td>
<td>12.5</td>
<td>25.4</td>
<td>23.8</td>
<td>0.0</td>
<td>414</td>
</tr>
<tr>
<td>d-SiCN:H #1</td>
<td>-</td>
<td>5.8</td>
<td>7.0</td>
<td>26.9</td>
<td>23.1</td>
<td>0.0</td>
<td>16.3</td>
<td>33.7</td>
</tr>
</tbody>
</table>

*a-SiOC:H #1* is p-SiOC:H#1 prior to UV treatment.
and unpaired electrons on carbon in a-C:H.) In these comparisons, we test the expectation that $\Delta g$ for a carbon dangling bond would be less than that of a silicon dangling bond. As shown in Fig. 4.10, in the case of a-Si:H, we observe a difference between high and low frequency line widths of about 7 Gauss (see Table 4.4). On the basis of this comparison, we measure a $\Delta g = 0.0041 \pm 0.0004$. The findings are reasonably consistent with previous studies of a-Si:H.\cite{61,62} The fast-passage traces\cite{50,60} on the same a-Si:H sample, as shown in Fig. 4.11, illustrate another potential advantage of very low frequency EDMR: at $\nu=353.5$ MHz, we are able to resolve superhyperfine interactions (i.e., those due to next-nearest neighbors) via fast-passage detection.\cite{50,60} The zero-crossing $g = 2.0055$ (measured at X-band) and superhyperfine splitting of 17 Gauss are also consistent with EPR measurements\cite{62} and ENDOR measurements\cite{63} indicating silicon dangling bond centers back-bonded to three silicon atoms. We observe a significantly different result in high/low frequency EDMR measurements on a-C:H samples. In this case, as illustrated in Fig. 4.12, we observe a change in line width of about 2 Gauss between X-band and low-field measurements. This result indicates that the a-C:H line width in both cases is dominated by unresolved hyperfine interactions, presumable due to nearby hydrogen atoms. The zero crossing $g$ of 2.0032 and line width of 9 Gauss are consistent with reports of spectra attributed to carbon dangling bond centers observed in EPR measurements of a-C:H and a-SiOC:H films.\cite{22,23,64} Finally, the measurements of $\Delta g = 0.0010 \pm 0.0004$ in a-C:H and $\Delta g = 0.0041 \pm 0.0004$ for a-Si:H provide a baseline measurement and a plausibility argument for the assignment of smaller $\Delta g$ to carbon dangling bonds and larger $\Delta g$ to silicon dangling bonds to be used throughout the rest of this study.
Table 4.4. A summary of EPR and EDMR results of a-SiOC:H films analyzed in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPR g</th>
<th>EDMR g</th>
<th>EPR LW, (G)</th>
<th>EDMR X-band LW, (G)</th>
<th>EDMR LF LW, (G)</th>
<th>Δg ±.0004</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H</td>
<td>NA</td>
<td>2.0055</td>
<td>NA</td>
<td>13</td>
<td>6.1</td>
<td>0.0041</td>
</tr>
<tr>
<td>a-C:H</td>
<td>NA</td>
<td>2.0032</td>
<td>NA</td>
<td>11</td>
<td>9.2</td>
<td>0.0011</td>
</tr>
<tr>
<td>d-SiOC:H #1</td>
<td>2.0025</td>
<td>2.0029</td>
<td>5</td>
<td>12</td>
<td>9.8</td>
<td>0.0012</td>
</tr>
<tr>
<td>d-SiOC:H #2</td>
<td>2.0028</td>
<td>2.0030</td>
<td>11</td>
<td>13</td>
<td>10.0</td>
<td>0.0018</td>
</tr>
<tr>
<td>p-SiOC:H #1</td>
<td>2.0031</td>
<td>2.0032</td>
<td>9</td>
<td>12</td>
<td>9.8</td>
<td>0.0013</td>
</tr>
<tr>
<td>p-SiOC:H #1</td>
<td>2.0030</td>
<td>2.0029</td>
<td>11</td>
<td>13</td>
<td>5.8</td>
<td>0.0048</td>
</tr>
<tr>
<td>d-SiCN:H #1</td>
<td>2.0026</td>
<td>2.0027</td>
<td>7</td>
<td>14</td>
<td>6.1</td>
<td>0.0047</td>
</tr>
</tbody>
</table>

*a-p-SiOC:H #1 is p-SiOC:H#1 prior to UV treatment.

b-Taken from Reference 22.

c-Taken from Reference 25.
Figure 4.10. Variable frequency EDMR in 10 nm a-Si:H. The X-band (bottom) and low-field (top) peak-to-peak line widths are 13 G and 6.1 G, respectively.
Figure 4.11. Fast-passage variable frequency EDMR spectra in 10 nm a-Si:H.
Figure 4.12. Variable frequency EDMR in 500 nm a-C:H. The X-band (bottom) and low-field (top) peak-to-peak line widths are 11 G and 9.2 G, respectively.
We have made SDTAT/EDMR measurements on two dense a-SiOC:H systems (i.e., d-SiOC:H#1 and d-SiOC:H#2) and one dense a-SiCN:H film. Table 4.4 provides a summary of EDMR results for films analyzed in this section. In the case of the dense and porous low-κ films, EDMR results are compared to EPR results as measured in similar films by our group in previous studies.[22,59] In the case of dense a-SiOC:H, X-band spectra are typically broad and featureless, with line widths ranging from 12-14 Gauss. EPR line widths in a-SiOC:H systems[22,23] are typically less broad than EDMR line widths observed in this study. This line width difference may be due to the detection of a wider variety of defects via EDMR than conventional EPR. It may also be a result of the detection differences via EDMR and EPR. However, the defects detected via both methods have virtually identical zero-crossing g values. The observation that the zero-crossing g values found via EDMR are the same as those found via EPR is a strong indication that the defects found via EPR and EDMR are the same. However, the difference in line widths of X-band EPR and EDMR measurements make this conclusion less than absolutely convincing.

Fig. 4.13 shows a comparison of EDMR spectra at X-band (9.5 GHz) and low-field (350 MHz) in d-SiOC:H#1. The zero-crossing g observed via EDMR (g = 2.0029 ± 0.0002) is within experimental error of the one observed via EPR (g = 2.0025 ± 0.0002)[22] strongly suggesting that defects detected via each respective technique are the same. The difference in the measured X-band line and low-field EDMR line widths, 12 Gauss and 9.8 Gauss, respectively, result in a measured Δg of 0.0012. Our measurement of Δg is virtually identical to the baseline measurements in a-C:H. This result, along with our previous EPR measurements in similar films, which suggest the presence of carbon dangling bonds in
Figure 4.13. Variable frequency EDMR in d-SiOC:H#1. The X-band (bottom) and low-field (top) peak-to-peak line widths are 12 G and 9.8 G, respectively.
similar films[11] and the similar nature of multiple frequency EDMR spectra of d-SiOC:H#1 to a-C:H, are collectively strong evidence for carbon dangling bond dominated conduction in d-SiOC:H#1.

Fig. 4.14 shows a comparison of high and low frequency EDMR measurements in d-SiOC:H#2. The line width at X-band, about 13 Gauss, and zero-crossing g = 2.0030 are both within experimental error of the X-band line width of d-SiOC:H#1. The change in line width from X-band to low-field, about 3 Gauss, is slightly larger for d-SiOC:H#2 than for d-SiOC:H#1. The resulting Δg = 0.0018 for d-SiOC:H#2. The Δg values for d-SiOC:H#1 and d-SiOC:H#2 (0.0012 and 0.0018, respectively) are within experimental error of one another. As for d-SiOC:H#1, FTIR measurements indicate a strong Si-O-Si bonding network in d-SiOC:H#2.[22] Thus, as in the case of d-SiOC:H#1, the similar nature of EDMR measurements in a-C:H, and evidence of carbon dangling bonds in similar films[22,23] provide strong evidence for carbon dangling bond mediated transport in d-SiOC:H#2.

Finally, high/low frequency EMDR measurements were performed on an a-SiCN:H film, as shown in Fig. 4.15. At X-band, the zero-crossing g = 2.0027 is, again, within experimental error of previous EPR measurements.[65] The change in EDMR line width from X-band to low-field is about 8 Gauss, resulting in a Δg = 0.0047. The much larger measured Δg = 0.0047 is probably too large to correspond to a carbon dangling bond, and matches fairly closely to our baseline measurements; we thus attribute these spectra to silicon dangling bonds. Silicon dangling bonds have previously been attributed to EPR spectra in a-SiCN:H films by Bittel et al.[65]
Figure 4.14. Variable frequency EDMR in d-SiOC:H#2. The X-band (bottom) and low-field (top) peak-to-peak line widths are 13 G and 10. G, respectively.
Figure 4.15. Variable frequency EDMR in d-SiCN:H#1. The X-band (bottom) and low-field (top) peak-to-peak line widths are 14 G and 6.1 G, respectively.
4.3 EDMR Study of Processing Effects upon p-SiOC:H Dielectrics

The nature of defects created by UV treatments, which are used to remove sacrificial porogens for the fabrication of porous low-κ a-SiOC:H films (i.e., p-SiOC:H) is not yet well understood and difficult to elucidate with conventional EPR studies, which are typically performed post-processing treatments.[22,23,58,59] By utilizing high/low frequency EDMR, as demonstrated in previous sections, we measure the breadth of $g$ tensor components before and after UV treatments to get a better understanding of the nature of defects generated by UV curing in nanoporous, ultra low-κ a-SiOC:H dielectrics.

Prior to UV curing, EDMR measurements, as shown in Fig. 4.16, reveal a difference in line width from X-band band to low-field of about 2 Gauss, resulting in a $\Delta g = 0.0013$. In addition, we observe a zero-crossing $g$ of 2.0032. All are within experimental error of baseline measurements of carbon defects in a-C:H. This suggests that carbon dangling bonds dominate transport phenomena prior to UV treatments, while the porogens are still fully intact. Our findings of carbon dangling bonds prior to UV treatments also suggest that porogen residues may not exclusively be responsible for carbon dangling bond mediated transport as suggested by earlier EPR studies of a-SiOC:H films post UV treatments.[22,27]

We note that EDMR measurements provided in this study do not rule out the presence of silicon dangling bonds at lower concentrations, which have been observed in similar films.[22,47]

After UV treatments, the EDMR response at X-band is, within experimental error, the same as that which was attributed by Pomorski et al. to so-called defect A.[22] The spectrum was dubbed defect A simply based upon the zero-crossing $g$ (2.0030) and large line width
Figure 4.16. Variable frequency EDMR in p-SiOC:H#1 prior to UV treatment. The X-band and low-field peak-to-peak line widths are 12 G and 9.8 G, respectively.
(11 Gauss),[22] which could be attributed to either a silicon or carbon dangling bond via conventional EPR measurements.

The EDMR responses at high and low frequencies post UV treatment are shown in Fig. 4.17. The X-band and low-field EDMR line widths indicate that $\Delta g = 0.0048$. This is likely too large to be a carbon dangling bond, and is consistent with our baseline measurements in a-Si:H. Thus, our results indicate that silicon dangling bonds play a dominant role in transport after a-SiOC:H exposure to UV radiation. This result is in agreement with previous suggestions that UV radiation damages both the Si-O-Si network and terminal Si-CH$_3$ bonding groups.[11,47,66,67] Though our results strongly indicate a dominating presence of silicon dangling bonds in transport, they do not rule out the presence of carbon dangling bonds present at lower concentrations. It has been shown that UV treatments sometimes leave behind porogen residue related carbon dangling bond defects, which may be reduced with remote H/He plasma treatments.[11,47,68]

To complement EDMR measurements in the porous a-SiOC:H films, we provide IV measurements pre and post UV treatments. IV curves pre and post UV treatments are shown in Fig. 4.18 at 400 K (the temperature at which EDMR measurements were taken) to illustrate the dramatic increase in dielectric leakage current post UV treatment. The EDMR amplitude after UV treatment (1.87 nA) is also significantly larger than prior to UV treatments (56.3 pA). Jointly, the EDMR and IV amplitudes pre and post UV treatment circumstantially indicate that network and/or terminal bonding may be damaged by UV treatments, generating silicon dangling bonds which play a dominating role in transport.

It has been suggested that silicon dangling bond energy levels are higher in the a-SiOC:H band gap than carbon dangling bond levels, which give rise to midgap states.[47]
Figure 4.17. Variable frequency EDMR in p-SiOC:H#1 post UV treatment. The X-band and low-field peak-to-peak line widths are 13 G and 5.8 G, respectively.
Figure 4.18. IV Curve of the porous a-SiOC:H film pre- and post-UV treatment at room temperature. The IV curve was taken at 400K for a direct comparison with EDMR measurements.
Thus, carbon dangling mediated transport would limit low-κ performance more than silicon dangling bonds due to lower barrier transport. In addition, TDDB studies of low-κ systems suggest that time-to-failure (TTF) decreases with increased carbon content.[68] We suggest that silicon dangling bonds and UV treatments should still be considered for more detailed modeling of low-κ reliability due to the connection between electronic transport and TDDB phenomena.
4.4 Development of Band Diagram Picture via EDMR and Other Characterization Techniques

In this section, we utilize the above results, in combination with band alignment measurements of a-SiCO:H ILD, a-SiCN:H Cu capping layer (CCL), and Ta(N) Cu barrier, and variable bias EDMR measurements to provide an understanding of defect energy levels, and a more complete band diagram picture including potential leakage paths. Note that the energy band gap of the ILD and CCL materials was calculated via REELS. Leakage from one Cu interconnect to another through the ILD or CCL, referred to as line-to-line leakage, is demonstrated in Fig. 4.19(a). Since the Ta/TaN barrier, which serves to prevent Cu diffusion into the low-κ ILD/CCL, makes physical contact with the ILD and CCL rather than the Cu, the band offsets between the TA(N) barrier and the ILD and CCL dielectrics are of interest. Using the method of Grant and Waldrop,[69] which relies on referencing the core levels of the dielectric to the valence band maximum and measuring the change of the position of the core levels at the low-κ/metal interface via x-ray photoelectron spectroscopy (XPS), the Schottky barriers were calculated as follows,

$$\Phi_B = E_g - (E_{CL})_{int} + (E_{CL} - E_V)_{bulk}. \tag{5.1}$$

Here, $\Phi_B$ is the Schottky barrier at the dielectric/metal interface, $E_g$ is the band gap of the dielectric, $(E_{CL})_{int}$ is the dielectric core level energy at the interface relative to the Fermi level, and $(E_{CL} - E_V)_{bulk}$ is the position of the dielectric core level relative to the valence band maximum measured at least 10 nm away from the interfaces. The Si 2p core level was used to determine $(E_{CL})_{int}$ and $(E_{CL} - E_V)_{bulk}$. A flat band diagram showing the Schottky barriers of the ILD and CCL including measured Schottky barriers are illustrated in Fig. 4.19(b). The Schottky barrier at the a-SiCN:H/Ta(N), $2.0 \pm 0.2$ eV, interface is much
smaller than that of the Ta(N)/a-SiOC:H barrier, 3.8 ± 0.2 eV. Thus, we expect that electron emission into the a-SiCN:H CCL will be the dominant leakage path when considering Schottky emission transport. For the case of transport through a-SiOC:H ILD, trap-assisted tunneling line-to-line leakage should be considered due to the fairly high energy barrier at the Ta(N)/a-SiOC:H interface. Later in this section, we will utilize EDMR to study trap-assisted tunneling through the a-SiOC:H ILD.

Another leakage mechanisms for the BEOL stack is referred to as layer-to-layer leakage, as demonstrated in Fig. 4.20(a). Layer-to-layer leakage entails tunneling from the Cu interconnect into the a-SiCN:H CCL, and subsequently into the a-SiOC:H ILD. Thus, we must now consider the valence band (or conduction band) offsets between the a-SiOC:H ILD and a-SiCN:H CCL materials. The method of Kraut[70] for indirectly references core levels via XPS was utilized. The method relies on referencing two distinct core levels in the two dielectric materials to their respect valence band maxima and then measuring the relative position of these core levels with respect to one another at their interface as follows:

$$\Delta E_V(SiCN:H/SiOC:H) = (E_{CL} - E_V)_{SiOC} - (E_{CL} - E_V)_{SiCN} + \Delta(E_{CL})_{int}, \quad (5.2)$$

where $\Delta E_V$ is the valence band offset between the two materials and $\Delta(E_{CL})_{int}$ is the relative position of the core levels in the two materials at the interface. The Schottky barrier between the Cu interconnect and the a-SiCN:H CCL was calculated using the method of Grant and Waldrop[61], as described above. The flat band diagram indicating the Schottky barrier at the Cu/a-SiCN:H interface and conduction band offset at the a-SiCN:H/a-SiOC:H interface is shown in Fig. 4.20(b). The point of least resistance, similarly to the case of line-to-line leakage, is at the metal/a-SiCN:H CCL interface. Thus, for layer-to-layer leakage,
we expect electron emission to predominantly occur into the a-SiCN:H CCL rather than the a-SiOC:H ILD.

For both line-to-line and layer-to-layer leakage, all of the interfacial barriers to electronic transport are large enough to satisfy the general rule of thumb established for the design of CMOS transistors with high-\( \kappa \) gate dielectrics; that is, the Si/gate dielectric interface offset must be > 1 eV.[71] Thus, based solely upon the band offsets shown above, we would not expect significant line-to-line or layer-to-layer leakage via Schottky emission. However, it is widely believed that defects and/or trap states play a role in electronic transport in these systems. In previous sections, we have showed that defect mediated transport through silicon and carbon dangling bonds is common in both porous and dense low-\( \kappa \) ILDs and CCLs.
Figure 4.19. (a) Schematic diagram illustrating two possible line-to-line leakage paths through low-κ ILD. (b) Schematic flat band diagram illustrating the barrier for electron injection (line-to-line leakage) from the Ta(N) Cu barrier into either a low-κ a-SiOC:H ILD or a low-κ a-SiCN:H CCL.
Figure 4.20. (a) Schematic flat band diagram illustrating the barrier for electron injection (layer-layer leakage) from Cu across the low-\(k\) a-SiCN:H CCL and low-\(k\) a-SiOC:H ILD. (b) Schematic flat band diagram illustrating the barrier for electron injection (layer-to-layer leakage) from Cu across the low-\(k\) a-SiCN:H CCL and low-\(k\) a-SiOC:H ILD.
Regarding the energy position of trap/defect states in low-\( k \) dielectrics, there have been fewer studies and most, at best, provide a plausible association with one of the specific defect states mentioned above. REELS studies by the authors of porous and non-porous low-\( k \) a-SiOC:H dielectrics have identified surface defects states with energy levels of \( \sim 5.2 \) and \( 7.0 \) eV created within the a-SiOC:H band-gap by Ar\(^+\) sputtering that were attributed to surface oxygen vacancy (i.e. silicon dangling bond) defect states [47]. Theoretical investigations of bulk Si dangling bond defects in SiO\(_2\) indicate that these states occupy a similar energy level in the bulk bandgap [72,73]. Thus, it is plausible to expect Si dangling bonds in the bulk of low-\( k \) a-SiOC:H dielectrics to occupy similar energy levels as at the surface.

Regarding carbon related defect states, detailed UVSE and REELS measurements reported by Urbanowicz [56,74] and the authors [47] have both shown that remnants of the organic porogen utilized to create nanoporosity in ultra low-\( k \) dielectric materials absorb broadly within the middle of the bandgap of the a-SiOC:H matrix. Although, the authors are unaware of any theoretical calculations regarding carbon or carbon dangling bond related defects in low-\( k \) a-SiOC:H or SiO\(_2\) like matrices, a few theoretical investigations of carbon cluster [75,76] and dangling bond defects at SiO\(_2\)/SiC interfaces have been reported [77,78]. For C-C pair defects on the SiO\(_2\) side of a SiO\(_2\)/SiC interface, these calculations indicate several possible defect states spanning the energy range of 2.5 – 7.5 eV within the SiO\(_2\) bandgap. These values are roughly in agreement with the values observed by UVSE and REELS for porogen residue defects in ultra low-\( k \) a-SiOC:H dielectrics. Recently, Guo has also shown using XPS that Ar\(^+\) sputtering of \( k = 2.3 – 3.3 \) a-SiOC:H dielectrics induces
surface bandgap narrowing due to the creation of carbon related states 1.3 – 2.2 eV above the a-SiOC:H valence band maximum [79].

To more definitively establish a correlation between electron transport in low-\(k\) a-SiOC:H dielectrics and specific defects, we have performed additional variable frequency EDMR measurements on Ti/7 nm \(k = 3.2\) a-SiO\(_{1.7}\)C\(_{0.8}\):H/p-Si capacitor structures. As shown in Fig. 4.20, the X-band (\(\nu = 9.5\) GHz) line width, about 13 Gauss, and zero-crossing \(g = 2.0030\) are both within experimental error of conventional X-band EPR measurements in similar systems [22]. The change in measured EDMR line width from X-band to low-frequency is about 3 Gauss, which, utilizing expression (4), yields \(\Delta g = 0.0018 \pm 0.0004\). The \(\Delta g\) for the a-SiO\(_{1.7}\)C\(_{0.8}\):H film, which is within experimental error of \(\Delta g\) measurements in a-C:H via variable frequency EDMR, suggests that the defects responsible for Fig. 4.21 are carbon dangling bond centers. The nature of EDMR measurements, which are exclusively sensitive to defects involved in transport, directly connects the carbon dangling bonds to electronic transport via SDTAT or related mechanisms.
Figure 4.21. Variable frequency EDMR in $k = 3.2$, a-$\text{SiO}_{1.7}\text{C}_{0.8}\text{H}$ measurements performed at a bias of -1 V [46]. The magnetic field axes are offset by the EPR centerfield, as defined in (3). The X-band and low-field peak-to-peak line widths are 13 G and 10. G, respectively. Here, the amplitudes are normalized for comparison.

The actual peak-to-peak amplitudes of the responses are about 5 pA.
To estimate the energy levels of the carbon dangling bond defects in the a-SiO$_{1.7}$C$_{0.8}$H system, we compare variable bias EDMR measurements with the band diagram for the a-SiOC:H capacitor structure. Fig. 4.22 shows EDMR amplitude ($\Delta I$) in a 7 nm a-SiO$_{1.7}$C$_{0.8}$H as a function of bias, and Fig. 4.23 shows the band diagrams for the same structure. For the band diagram simulations, the band gap of the a-SiO$_{1.7}$C$_{0.8}$H film was taken to be 8.2 eV, corresponding to prior REELS measurements. Since the $\Phi_B$ and VBO for the Ti/a-SiO$_{1.7}$C$_{0.8}$H and a-SiO$_{1.7}$C$_{0.8}$H/p-Si interfaces are unknown, the reported band alignments for Ti/SiO$_2$ and SiO$_2$/p-Si interfaces were used instead [80]. This is partly justified by prior IPE measurements performed by Atkin where the VBO for a $k = 2.4$ a-SiOC:H/Si interface was found to be 4.1 eV, virtually identical to that for a SiO$_2$/Si interface (4.0 eV) [81].

Note that EPR measurements in these films have indicated that the defect concentration is about $2 \times 10^{17}$ defects/cm$^3$. This defect concentration roughly corresponds to an average defect separation of about 15 nm. Thus, we’d expect that tunneling will predominately occur through one defect center through the middle of the a-SiOC:H band gap [82], where tunneling would most effectively occur. In our very crude model, we assume that near middle of the dielectric bandgap defects dominate due to trap assisted tunneling. The black circle in each band diagram represents the approximate defect energy levels which are consistent with the EDMR measurements. It should be emphasized that our analysis of defect energy levels in this study are necessarily rather crude, providing only a rough measure of defect energy level locations, rather than exact defect energy levels. Nevertheless, the crude model provides a semi-quantitative explanation of the results, and a rough measure of the defect energy levels. In the case of thicker low-$k$
dielectrics, such as those used for BEOL ILDs, it is likely that the tunneling process would occur through multiple defects. This process is referred to as variable range hopping [83], and has been previously observed in low-$k$ dielectrics [46,84].
Figure 4.22. Variable bias EDMR in a-SiO$_{1.7}$C$_{0.8}$:H taken at X-band (9.5 GHz). $\Delta I$ refers to the peak-to-peak amplitude of the X-band response in Fig. 10.
Figure 4.23. Simulated band diagrams for the Ti/ a-SiO$_{1.7}$C$_{0.8}$:H /p-Si system at various biases [80]. The band gap of the a-SiO$_{1.7}$C$_{0.8}$:H dielectric is 8.2 eV. The black dot in the dielectric band gap corresponds to the approximate defect energy levels which we estimate from variable bias EDMR measurements.
Fig. 4.22 shows that the delta I response turns on at small negative biases. At these small biases, the band diagrams of Fig. 4.23 indicate that (less than or equal to 750 mV) the metal Fermi energy has not yet crossed the level of the silicon conduction band edge. If the defect levels detected in the EDMR response are located approximately as indicated by the large dot in the Fig. 4.23 band diagrams, the EDMR response would inevitably be small at such small magnitude negative voltages because the electrons tunneling through the carbon dangling bond defect levels would encounter the very nearly empty silicon band gap. However, as the magnitude of the negative dielectric bias is increased, the metal Fermi level approaches and surpasses the silicon conduction band, allowing for tunneling events through the carbon dangling bonds into abundant states in the silicon conduction band. The ΔI response begins to saturate at about -2.5 Volts. This likely indicates that the range of defect energy levels is not extremely broad, and suggests the possibility that there may be a diamagnetic level separated by the electron-electron correlation energy. No response is detected at positive biases. At positive biases, the response is not detected because the defect levels are below the metal Fermi energy, and there are no states available for tunneling into the metal. Thus, our multiple frequency and variable bias EDMR measurements jointly indicate that there are carbon dangling bond centers near the middle part of the a-SiOC:H band gap.

Unfortunately, relatively few investigations of trap/defect states in low-\(k\) CCL class materials exist. To date, both Kobayashi [85] and Bittel [58] have utilized EPR to investigate paramagnetic defect centers in low-\(k\) a-SiCN:H CCLs with \(k\) values ranging from 4.8 to 6.5. Both reported paramagnetic defects with \(g\)-values that were consistent with silicon dangling bond K centers observed in a-SiN:H. Bittel further showed that the density
of Si dangling bond centers and leakage currents in a-SiCN:H both decreased substantially with nitrogen content. The former is consistent with the Si dangling bond assignment, whereas the latter suggests that attention to stoichiometry is important for minimizing both trap/defects and leakage currents in a-SiCN:H CCL films.

For low-\(k\) a-SiC:H CCLs, a detailed EPR investigation by Pomorski, in contrast, determined that carbon dangling bond defects were the dominant paramagnetic defects for stoichiometric films. This study also showed a strong correlation between electrical leakage and paramagnetic defects and a strong correlation between hydrogen content and spin defect density. The former is consistent with prior observations for both low-\(k\) a-SiOC:H ILDs and low-\(k\) a-SiCN:H CCLs while the latter correlation is consistent with the ability of hydrogen to passivate dangling bond defects. Interestingly, a strong correlation between sp\(^2\) carbon clusters, EPR carbon dangling bond defects, and electrical leakage has also been observed in bulk polymer derived a-SiC:H and a-SiCN:H ceramics. Additional studies have also found low-\(k\) CCL materials to be sensitive to creation of additional trap/defect states by exposure to various forms of UV and ionizing radiation.

Fortunately, substantially more is known regarding the energy levels of trap/defect states in a-SiN:H and a-SiC:H CCL materials thanks to several prior studies investigating their properties for use in a variety of non-volatile memory, optoelectronic, and photovoltaic devices. For stoichiometric a-Si\(_3\)N\(_4\), theoretical calculations by Robertson have shown that silicon dangling bonds introduce states in the mid to mid-upper portion of the bandgap, while nitrogen dangling bond states lie within the top of the valence band. The presence of non-stoichiometry, as is common in PECVD a-SiN\(_x\):H
CCLs, can introduce Si-Si states that lie closer to mid-gap for Si rich stoichiometries and can lead to significant bandgap narrowing for \( x < 1.2 \) [94-96]. Similarly, N dangling bond states can rise above the valence band maximum for nitrogen rich stoichiometries [94-96]. This picture has largely been confirmed experimentally by a combination of EPR, XPS, and related techniques [97-104].

For stoichiometric a-SiC:H, analogous theoretical calculations by Robertson have shown that Si dangling bond levels similarly lie below the conduction band minimum at \( \sim 2 \) eV within the bandgap [105]. In contrast, \( \text{sp}^3 \) carbon dangling bond states reside closer to mid-gap at \( \sim 0.6 – 1.2 \) eV. For non-stoichiometric a-Si\(_{1-x}\)C\(_x\):H, Si-Si states in Si rich films introduce states just above and below the VBM and CBM, respectively, that effectively lead to bandgap narrowing as carbon content is decreased. For carbon rich a-Si\(_{1-x}\)C\(_x\):H films, \( \text{sp}^2 \) carbon clusters are predicted to form that create bonding and antibonding states that define the bandgap for \( x > 0.6 \). As for a-SiN:H, the above picture has also been largely confirmed experimentally by a combination of ESR, XPS, and other techniques [106-112].

To more definitively establish a correlation between electron transport in low-\( k \) a-SiCN:H CCL materials and specific defects, we have again performed variable frequency EDMR measurements using Ti /5-10 nm \( k = 5.8 \) a-SiC\(_{0.6}\)N\(_{0.5}\):H /p-Si capacitor structures. EDMR spectra at X-band \( (\nu = 9.5 \) GHz) and low-frequency \( (\nu = 350 \) MHz) are shown in Fig. 4.24. The zero-crossing \( g = 2.0027 \) is within experimental error of conventional X-band EPR measurements in these systems [25]. The change in line width from X-band to low-frequency is about 8 Gauss, resulting in a \( \Delta g = 0.0047 \pm .0004 \). This \( \Delta g \) is too large to
be a carbon dangling bond, and is fairly close to multiple frequency EDMR measurements in a-Si:H [46]. Thus, we attribute the EDMR spectra shown in Fig. 4.24 to silicon dangling bonds. This definitively establishes that the Si dangling bonds previously detected by Kobayashi [85] and Bittel [58] using EPR are directly involved in electrical transport through a-SiCN:H CCL materials.

![EDMR Spectrum](image)

Figure 4.24. Variable frequency EDMR in a-SiCN:H measurements performed at a bias of -3 V [46]. The magnetic field axes are offset by the EPR center field, as defined in (3). The X-band and low-field peak-to-peak line widths are 14 G and 6.1 G, respectively. Here, the amplitudes are normalized for comparison. The actual peak-to-peak amplitudes are about 60 pA.
To estimate defect energy levels in the same $k = 5.8 \text{ a-SiC}_{0.6}\text{N}_{0.5}:\text{H}$ film, we measured $\Delta I$ as a function of bias using the same capacitor structures (see Fig. 4.25). For simulations, the $\text{a-SiC}_{0.6}\text{N}_{0.5}:\text{H}$ band gap was taken to be 3.2 eV and, based on arguments similarly used for Ti/SiOC:H/Si, previous reports for the Ti/SiN:H and SiN:H/Si interfacial band alignments were used. In this case, EDMR was detected at both polarities, but the $\Delta I$ response was again anisotropic. The $\Delta I$ response was compared with band diagrams that are shown in Fig. 4.26 [80]. As for the case of EDMR in the 7 nm a-SiOC:H film in section 3.5, one would expect to see the most effective tunneling through just one defect in the middle of the dielectric. In the negative biasing regime, the response is detected at biases as small as -1 V. This is consistent with paramagnetic levels near the middle/upper-middle part of the a-SiCN:H band gap. The black circles in Fig. 4.26 indicate such levels. The $\Delta I$ response increases through biases of roughly -3 V, as the metal Fermi energy is swept through the upper part of the a-SiCN:H band gap.

In the positive biasing regime, the $\Delta I$ response does not turn on until about 2 V. At positive voltages, the defect levels are opposite the silicon band gap, as shown in Fig. 4.26. Thus, there are no states available to provide the tunneling current into the defects. However, when the defect levels cross the silicon valence band maximum, the high density of valence band electrons become available and provides an abundant source of electrons for tunneling through defect levels. The response saturates at both polarities, again suggesting that the defects contributing to the SDTAT do not extend high into the dielectric band gap. These results thus indicate that silicon dangling bond centers with energy levels in the upper part of the band gap play an important role in electrical transport through a-SiCN:H CCL class materials.
Figure 4.25. Variable Bias EDMR in d-SiCN:H taken at X-band (9.5 GHz). ΔI refers to the peak-to-peak amplitude of the X-band response in Fig. 13.
Figure 4.26. Simulated band diagrams for the Ti/$k = 5.8$ SiC$_{0.6}$N$_{0.5}$:H#1/p-Si system at various biases [80]. The band gap of the $k = 5.8$ SiC$_{0.6}$N$_{0.5}$:H1 is 3.2 eV. The black dot in the dielectric band gap corresponds to the approximate defect energy levels we estimate for the measurements.
Having reviewed the variety of different defect and trap states observed in both low-$k$ ILD and CCL materials and established a definitive connection between electron transport through these defects via variable frequency EDMR, we next update our line-line and layer-layer leakage band diagrams with the rough energy level determined for each class of defect as shown in Fig. 4.27 and 4.28, respectively. From Fig. 4.27, it can be seen that carbon dangling bond and carbon cluster/porogen residue defects in both the low-$k$ ILD and CCL layers generally align with the Fermi level of the Ta(N) electrode. Based on this observation, one would anticipate that electrical leakage through either dielectric would likely occur through such defects if present. This is consistent with the EDMR measurements described here on a $k = 3.2$ a-SiOC:H dielectric and prior measurements by Pomorski on low-$k$ a-SiC:H CCL class materials.[23] However, for a-SiCN:H CCL materials, EPR and EDMR both point to silicon dangling bonds being more prominent and involved in electrical transport. This indicates that while carbon is present in a-SiCN:H CCL materials, the deposition method and process chemistries utilized must favor conditions that minimize carbon cluster or dangling bond formation and lead instead to a predominance of silicon dangling bond defects.
Figure 4.27. Schematic flat band diagram (with relevant defect/trap positions added) illustrating the barrier for electron injection (line-line leakage) from the Ta(N) Cu barrier into either a low-\(k\) a-SiOC:H ILD or a low-\(k\) a-SiCN:H CCL.
Figure 4.28. Schematic flat band diagram (with relevant defect/trap positions added) illustrating the barrier for electron injection (layer-layer leakage) from Cu and across the low-\( k \) a-SiCN:H CCL and low-\( k \) a-SiOC:H ILD.
The above defect band alignment diagrams can now be utilized to rationalize the results of several prior investigations of leakage mechanisms in integrated low-\(k\)/Cu interconnect structures. In many cases, attempts have been made to deduce both the leakage mechanism and interfacial or trap barrier height via a detailed analysis of the current-voltage (IV) characteristics from a low-\(k\) metal-insulator-metal (MIM) or metal-insulator-semiconductor (MIS) structure [113-117]. In essentially all cases, the barrier heights deduced from the IV analysis have been a small fraction of the IPE or XPS interfacial barrier heights shown above [118]. This discrepancy can now be understood by considering both the dominant trap/defect state likely to be present and its energy level within the low-\(k\) dielectric.

As one example, Ngwan determined a barrier height of 0.69 eV for trap mediated FP leakage at a a-SiN:H CCL (\(k=6.9\))/a-SiOC:H ILD (\(k=2.9\)) interface in a Cu comb capacitor structure [114]. This barrier height is substantially less than the \(\sim 2\) eV interfacial Schottky barrier determined by XPS for a-SiN:/Ta interfaces [119]. Based on Fig. 4.28, the barrier height deduced by Ngwan, however, is consistent with the barrier or trap height that would be expected if electron transport were to occur through the a-SiN:H CCL via Si dangling bond states which as previously discussed have been shown to be the dominant paramagnetic defect in a-SiN:H [92-96]. In this regard, the FP barrier height of 0.69 eV reported by Ngwan is fully consistent with prior investigations of electron transport in PECVD a-SiN\(_x\):H dielectrics where FP leakage with barrier heights of 0.5 – 1.0 eV have been frequently reported for films with \(x\) ranging from 0.5 – 1.3 [110-112].

As another example, several investigations of electrical leakage in MIM and MIS structures with \(k = 2.5 - 2.9\) ILDs have reported Schottky emission (SE) based leakage
with interfacial barrier heights on the order of 0.7 – 1.0 eV [113-116]. These values are substantially smaller than the interfacial barriers of 4 – 5 eV determined by XPS and IPE [81]. In this case, the greatly reduced interfacial barriers determined electrically can be rationalized by consideration of the likely presence of mid-gap carbon dangling bond defects in the low-\(k\) ILD. As mentioned previously, several prior studies have established a strong correlation between electrical leakage in low-\(k\) a-SiOC:H ILDs and the concentration of carbon dangling bond defects or carbon related porogen residues [22,120].

A final and more speculative example concerns the recent investigation by Wu of electrical leakage in a \(k = 2.0, 46\%\) porous a-SiOC:H ILD [117]. In contrast to several prior investigations of lower porosity, \(k = 2.5 – 2.9\) ILDs where PF leakage has been predominantly reported, Wu observed for the substantially lower \(k\), higher porosity ILD an exponential power law current density vs. electric field dependence at fields of 1 – 4 MV/cm. This dependence was determined to be consistent with a trap limited, space-charge-limited current (SCLC) leakage mechanism. The high exponent of the observed power law dependence was attributed to the filling of an exponential distribution of trap states with the maximum density at the band edge. At fields > 5 MV/cm, Wu further observed a transition to trap-assisted tunneling (TAT) followed by Fowler-Nordheim (FN) tunneling. Additional detailed analysis deduced barrier heights of 2.4 and 4.2 eV for TAT and FN leakage, respectively. This distinctive behavior can be understood via consideration of both the unique processing the low-\(k\) ILD received and the defect enriched low-\(k\) ILD band diagram shown in Fig. 4.28. For the former, a remote \(H_2\) plasma cure was employed prior to standard UV curing to more efficiently remove the organic porogen and optimize mechanical properties [121]. Prior UVSE measurements reported by Baklanov have shown
that porous low-$k$ ILDs cured in this manner exhibit zero traces of porogen residues in the bandgap [122]. Further, EPR measurements reported by Pomorski also show a near complete absence of carbon dangling bond defects, and in contrast show a broad defect center that has been tentatively attributed to a Si dangling bond [23]. Thus, the low-field SCLC leakage observed by Wu is consistent with the likely absence of mid-gap carbon related defect states. Also, the high field TAT based leakage with a barrier height of 2.4 eV is consistent with transport through Si dangling bonds where Fig. 4.22 indicates these defects should lie at a similar energy level.
4.5 References


Chapter 5

SPIN-TRANSPORT, MAGNETORESISTANCE, AND ELECTRICALLY DETECTED MAGNETIC RESONANCE IN AMORPHOUS HYDROGENATED SILICON NITRIDE

5.1 Introduction

Amorphous hydrogenated silicon nitride (a-SiN:H) is an important material in solid state electronics; it has long been used as a passivation layer in solar cells,[1] and a gate dielectric in thin-film transistors used for liquid crystal displays.[2,3] Electronic transport in a-SiN:H is of renewed interest due to potential applications in standalone and embedded memory applications.[4-7] However, a detailed atomic-scale understanding of electronic transport in these materials, especially in thin films at fairly low electric fields, is far from complete. We utilize EDMR via SDTAT, to understand defect chemistry and energy levels in 3 nm a-SiN:H dielectric films.

By comparing EDMR and MR amplitudes over a wide range of Ti/a-SiN:H/p-Si capacitor biasing conditions with metal/insulator/semiconductor band diagrams, we establish a connection between defect energy levels for each measurement technique. The very close correlation between the EDMR and MR responses provides strong evidence linking defects observed through the EDMR to MR responses in a-SiN:H films. As near-zero field MR phenomena are of great interest in a variety of systems for spintronic applications,[8,12,14-16] our approach for the study of defect-mediated spin-transport may be of broader interest in that it may contribute to understanding MR phenomena in a variety of amorphous organic and inorganic dielectrics. This strategy for approximating defect energy levels via EDMR has been previously demonstrated in silicon oxynitride[17] and
low-κ dielectric[18] films. By comparing EDMR and MR amplitudes over a wide range of Ti/a-SiN:H/p-Si capacitor biasing conditions with metal/insulator/semiconductor band diagrams, we establish a connection between defect energy levels for each measurement technique. The very close correlation between the EDMR and MR responses provides strong evidence linking defects observed through the EDMR to MR responses in a-SiN:H films. As near-zero field MR phenomena are of great interest in a variety of systems for spintronic applications,[8,12,14-16] our approach for the study of defect-mediated spin-transport may be of broader interest in that it may contribute to understanding MR phenomena in a variety of amorphous organic and inorganic dielectrics. This strategy for approximating defect energy levels via EDMR has been previously demonstrated in silicon oxynitride[17] and low-κ dielectric[18] films.

In addition, we perform EDMR at multiple frequencies. Multiple frequency EDMR measurements can sometimes be useful for understanding defect chemistry when featureless spectra are present.[19] This is so because the multiple frequency measurements provide information about the range of defect $g$ tensor components, which reflects the defect’s spin-orbit coupling. The measure of spin-orbit coupling is also of interest for understanding spin-relaxation mechanisms in both organic and inorganic films of interest for spintronic devices.[11]

The electron paramagnetic resonance (EPR) response of a-SiN:H is usually dominated by a silicon dangling bond center in which the central silicon is back-bonded to three nitrogen atoms; the defect is referred to as the K center.[20-22] Although the K center concentration is generally quite high, its role in electronic transport has not been clearly established. The dominance of a single paramagnetic defect suggests that silicon nitride
could provide a simple model system for the study of low field electronic transport in highly defective amorphous insulators via magnetic resonance. In this chapter, we utilize EDMR to link defects to spin-transport phenomena and MR phenomena in a-SiN:H.

5.2 Experimental Details

EDMR and MR measurements were performed on 3 nm thick a-SiN:H MIS structures with p-Si substrates and Ti/Al gates. The a-SiN:H film was deposited at 400°C via plasma enhanced chemical vapor deposition (PECVD) using silane (SiH₄) and ammonia (NH₃) as process gases.[26] Combined Rutherford backscattering (RBS) and nuclear reaction analysis (NRA) measurements indicated a N/Si ratio of ≅ 1.4 and hydrogen content of 23±5%.[27] The refractive index (at 630 nm) was determined to be 1.74 via spectroscopic ellipsometry and the low frequency (0.1 MHz) dielectric constant was determined to be 6.8 via capacitance-voltage measurements performed using an Hg prober. EDMR measurements were made at X-band (ν = 9.103 GHz) as well as low frequencies (ν = 151.0 MHz and ν = 353.5 MHz) on home-built EDMR spectrometers. The amplitudes of the RF fields (Bₑ) were about 0.2 Gauss in both low field/frequency cases, and about 0.1 Gauss at X-band. MR measurements were also performed with and without the applied RF fields. (The MR response was not altered by the RF field.) EDMR and MR measurements were made with Ti/Al gates biased from -2.5 volts to 3.0 volts. EDMR and MR measurements were conducted between 290 K and 400 K.

5.3 EDMR and MR in a-SiN:H

Fig. 5.1 illustrates representative room temperature EDMR responses at (a) 151.0 MHz, (b) 353.5 MHz, and (c) 9.103 GHz. In all cases, a strong single line spectrum was observed.
The zero-crossing $g$ was obtained for the spectrum in Fig. 5.1 (c) taken at 9.103 GHz. The line width at this frequency is 13 Gauss. The X-band zero-crossing $g$ and the line width are both independent of orientation, strongly suggesting that the EDMR spectrum is due to a defect within the a-SiN:H, rather than at the p-Si/a-SiN:H interface. The X-band EDMR line width and zero-crossing $g$ (2.0029 ± 0.0003) are also both consistent with the observed line width and zero-crossing $g$ of the K center, which has been reported to have a zero-crossing $g \approx 2.003$ and X-band line width of about 13 Gauss.[17,20-22] The K center is a silicon dangling bond center in which the central silicon is back-bonded to three nitrogen atoms.[17,20-22]

Fig. 5.2(a) illustrates a wider scan measurement which involves both EDMR and MR taken with an RF frequency of 151 MHz. The EDMR responses, which satisfy the EPR condition, occur at ±55 Gauss, whereas the MR response is centered about zero field. The resonance at 55 Gauss is consistent with expression (1) and $g = 2.00$; a more precise measure of $g$ is not possible in our low-field measurement. Note the approximately equal magnitudes for the MR and EDMR responses.
Figure 5.1. EDMR responses in a-SiN:H at (a) $\nu = 151.0$ MHz, (b) $\nu = 353.5$ MHz, and (c) $\nu = 9.103$ GHz. In each case, the spectrum is offset by the magnitude of the resonance field; that is, the 9.103 GHz resonant field of 3250 Gauss is offset by 3250 Gauss. The line widths for (a), (b) and (c) are 5.7 Gauss, 6.0 Gauss, and 13 Gauss, respectively.
Figure 5.2. (a), RF on (ν = 151.0 MHz): EDMR spectra centered at about ±55 Gauss and near zero field MR in 3 nm a-SiN:H. (b), RF turned off: near zero field MR only.
Fig. 5.2(b) was taken with all of the settings the same as in Fig. 5.2(a) except that the RF was turned off. Fig. 5.3 illustrates the near zero field MR and EDMR amplitudes, $\Delta I/I$, taken at $\nu = 151.0$ MHz. Here, $\Delta I$ is the change in current due to the EDMR or MR responses, and $I$ is the total device current. Note that the EDMR and MR amplitude versus bias responses are very nearly identical. Both are sharply spiked at a very small magnitude of gate potential. Both drop off sharply with increasing negative gate bias magnitude, and, in both cases, no response is observed at any positive gate bias. We interpret these results in terms of the series of band diagrams illustrated in Fig. 5.4. Since defect sites must be paramagnetic to play a role in EDMR, the very sharp turn on of the EDMR response at very low negative voltages and the substantial drop in $\Delta I/I$ at larger negative biases indicates that the metal Fermi energy must cross a dominating paramagnetic defect level at a bias of about -100 mV, where the peak of the $\Delta I/I$ response is observed. At -100 mV, the metal Fermi energy is approximately 3.1 eV above the a-SiN:H valence band edge, which indicates that the dominating defect level is also about 3.1 eV above the a-SiN:H valence band edge. This is in agreement with previous calculations of K center energy levels in a-SiN:H.[29] The steep drop in $\Delta I/I$ suggests that at a slightly higher Fermi level, the spin-dependent process is, to a large extent, extinguished, and that the DC current increases as the metal Fermi energy crosses the semiconductor conduction band edge, increasing the probability of direct tunneling thus decreasing $\Delta I/I$. Such a result could be anticipated by two levels closely spaced in energy around the middle of the a-SiN:H band gap, corresponding to a $+/0$ transition of a dangling bond defect rendering the center paramagnetic and a slightly higher second level corresponding to a $0/-$ transition rendering the defect diamagnetic and unable
to contribute to a SDTAT event. Such behavior has been reported previously in K center-like defects in silicon oxynitride.[17]

![Graph](image)

Figure 5.3. EDMR (orange circles) and MR (blue squares) responses normalized to total tunneling current as a function of bias voltage in 3 nm a-SiN:H.
Figure 5.4. Simulated band diagrams of the metal/a-SiN:H/p-Si stack at various biases. The black dots represent approximate defect energy levels. Band diagrams were simulated using the Boise State Energy Band Diagram Program (see Ref. 34).
In the positive biasing scheme, EDMR and MR responses are not detected. This result is also consistent with two K center levels with a small electron correlation energy. Previous findings in silicon nitride\(^{29}\) and silicon oxynitride\(^{17}\) have indicated a K center correlation energy of about 200 meV. The sharp \(\Delta I/I\) response observed in Fig. 5.3 is qualitatively consistent with previous findings. With small positive bias, the K centers do not take part in trap assisted tunneling because essentially no states are available to tunnel from the p-Si band gap into the single paramagnetic K center. At larger positive biases, the semiconductor valence band crosses the defect energy level, and tunneling into the K center should be considered. However, as shown in Fig. 5.4 at 2 V, the p-Si Fermi level is far above the paramagnetic K center level, which would render the dangling bond orbital doubly occupied and thus diamagnetic. Thus, we would expect that the SDTAT response would be absent, as observed.

Additional evidence linking the EDMR and MR response is illustrated by Fig. 5.5, which shows a near identical correspondence between the EDMR and MR amplitudes versus temperature. Both responses are substantially larger at higher temperature, likely indicating that both are a result of defect-mediated hopping phenomena. Since our film thickness is just 3 nm, we expect tunneling to predominantly occur through a single defect. (The SDTAT process in this study is slightly different than variable range hopping, which typically involves hopping of electrons through multiple defects.\(^{30,31}\))
Figure 5.5. EDMR (orange circles) and MR (blue squares) amplitudes (ΔI) as a functions of temperature. Lines are to guide the eye.
An evaluation of the range of $g$ tensor parameters may be obtained from a comparison of EDMR measurements at multiple frequencies, as discussed in Chapter 2. Recall, from Chapter, the frequency dependence of the breadth of $g$ tensor components,

$$\Delta g \approx \frac{4\beta}{\hbar} \left( \frac{\Delta H_{high} - \Delta H_{low}}{v_{high}} \right).$$

(5.1)

Using high (9.1 GHz) and low frequency (150 MHz – 350 MHz) EDMR, and (6), we measure $\Delta g = 0.0042 \pm 0.0004$. Note that our measure of $\Delta g$ is approximate since we are not observing actual ‘powder patterns,’ but rather featureless spectra in which the powder pattern is obscured, presumably by unresolved hyperfine interactions. By itself, the measure of $\Delta g$ is usually not conclusive, but it can be quite useful for assigning defect structure. If the $g$ tensor components are already known, there is an obvious diagnostic capability. If the $g$ tensor components are not known, the observation is still helpful, but a straightforward analysis may not be available. For example, an E’ center (silicon back-bonded to three oxygens) exhibits $\Delta g = 0.0014$,\,[32] and a silicon dangling bond in a-Si:H exhibits $\Delta g = 0.004$.\,[19,33]

### 5.4 Summary

In summary, we observe a very close correspondence between EDMR and MR amplitudes as a function of bias, indicating a closely related physical origin. Our results indicate that EDMR and MR phenomena in this study are due to spin dependent tunneling transport through K centers which are about 3.1 eV above the a-SiN:H conduction band edge. The sharp EDMR and MR responses versus bias indicate a small correlation energy, consistent with previous findings which indicate a correlation energy of about 200 meV.\,[17] Additionally, we utilize variable frequency EDMR to estimate the K center $\Delta g = 0.0042 \pm$
0.0002. (The K center defect \( g \) tensor components are obscured by hyperfine interactions in conventional magnetic resonance spectra.)
5.5 References


Chapter 6

ON THE UBIQUITOUS NATURE OF MAGNETORESISTANCE IN AMORPHOUS SEMICONDUCTORS AND DIELECTRICS

6.1 Introduction

Magnetoresistance (MR) phenomena are of great technological interest for potential spintronic applications in a variety of materials systems.[1-8] In this section, we report on near-zero field MR phenomena in a variety of amorphous systems including a-Si:H, a-C:H, a-SiC:H, a-B:H, a-SiOC:H, and a-SiCN:H. The materials analyzed in this study are already utilized in a wide range of applications including thin-film transistors,[9,10] and low-dielectric constant materials for microprocessors.[11-15] We show that spin-transport MR phenomena in these materials are ubiquitous and should be of interest for potential spintronic applications. In addition, near-zero field MR phenomena may be useful for understanding defect chemistry and energy levels in these systems. To better understand the nature of transport phenomena and the nature of point defects responsible for spin-dependent transport phenomena, we utilize electrically detected magnetic resonance (EDMR), a derivative of electron paramagnetic resonance (EPR). Due to its sensitivity and analytical power, EDMR has gained popularity for studying paramagnetic centers responsible for performance limitations in a variety of electronic materials. Spin dependent trap assisted tunneling (SDTAT) EDMR phenomena in a variety of amorphous semiconductors and dielectrics has been reported, and can be a useful method for understanding defect chemistry and electronic transport in a variety of systems as previously explained in this work.[8,14-17] Performing EDMR at multiple EPR frequencies (≈ 100 MHz and ≈ 9.5 GHz) allows for an understanding of contributions to
featureless spectra line widths, and thus local defect structure. (For a detailed discussion regarding the theory and utility multiple frequency EDMR, see Refs. 8 and 15 and Chapter 2.) EDMR measurements performed on Ti/amorphous insulator (semiconductor)/p-Si capacitors as a function of capacitor bias, and thus electric field, provide an estimate of energy level locations. (This variable bias EDMR technique has also been previously demonstrated in a variety of dielectrics.)[8,14,17] Comparisons of EDMR and MR amplitudes allow for a strong connection between defects responsible for the near-zero field MR response.

### 6.2 Experimental Details

EDMR and MR measurements in this study were made on several commercial and home-built spectrometers. X-band EDMR measurements were made on a homemade EDMR spectrometer which includes a 4 inch Lakeshore electromagnet with a Micro-Now X-band microwave bridge and TE$_{102}$ cavity. In order to accurately measure magnetic field, we utilize an NMR Gaussmeter. Low-field EDMR measurements were performed on home-built EDMR spectrometers. In the low-frequency EDMR measurements, an RF frequency magnetic field is supplied by a Stanford Research Systems signal generator and a Doty Scientific RF coil and tuning circuit. Unless otherwise specified, measurements were performed at room temperature unless otherwise specified.

Amorphous films in this study were deposited on 300 mm diameter Si (001) wafers with a native oxide via plasma enhanced chemical vapor deposition with a variety of commercially available precursors in combination with diluent gases such as He, H$_2$, CO$_2$, N$_2$, and NH$_3$. Table 6.1 summarizes the precursors, dielectric constant ($\kappa$), band gap, thickness, and compositions of the films analyzed in this study.
6.3 Magnetoresistance Observations in Amorphous Semiconductors and Dielectrics

Fig. 6.1 shows representative MR and EDMR spectra in a-C:H, a-B:H, a-Si:H, a-SiCN:H, and a-SiC:H taken at -5 V, 4 V, -1.5 V, -3 V, and -3 V, respectively. Biases were chosen based upon optimal signal-noise ratio. Spectra shown in Fig. 6.1 have been grouped together simply due to similar spectra shape. The EDMR response may be turned on via an RF coil, in this case at 350 MHz, as shown in Fig. 6.1 (b). The RF response does not seem to affect the amplitude or line width of the zero-field MR response in any case. The line widths of the zero-field MR responses in Fig. 6.1 vary widely from 17.2 Gauss in a-Si:H to 102 Gauss in a-B:H. (A summary of MR and EDMR results may be found in Table 6.2.) Note that the line widths of the EDMR and MR responses in the films analyzed in Fig. 6.1 are different by a factor of about 3 (excluding a-B:H, for which the MR line width is a factor of 17 larger than the EDMR response). A variety of line broadening mechanisms and relaxation mechanisms have been suggested for MR phenomena in organic and inorganic systems.[5-7,18] Recall from Chapter 2 that the EDMR and MR responses are fundamentally different. The EDMR response is due to transformations between singlet and triplet states at the EPR condition, while MR responses occur via singlet/triplet mixing near zero-magnetic field. In MR, singlet/triplet mixing becomes increasingly probable as the quantization axis of the electron spins approaches the local hyperfine field.[2,6] For results in Fig. 6.1, there is no notable correlation between our measured $\Delta g$ values (see Table 6.1), and MR line widths. This is in agreement with suggestions that local hyperfine fields, rather than spin-orbit coupling, dominate the MR line width.[5-7]

In simple cases, such as a-Si:H or a-C:H, it may be fairly easy to understand the nature of MR responses from EDMR measurements at multiple frequencies and biases. For
example, the authors have previously shown that SDTAT through silicon and carbon dangling bonds are responsible for EDMR spectra in the a-Si:H films and a-C:H which are utilized in this study, respectively.[15] In this study, we demonstrate that MR responses may also be detected in the a-Si:H films a-C:H. EDMR and MR amplitudes are compared in Figs. 6.2 and 6.3 at multiple Ti/a-Si:H/p-Si and Ti/a-C:H/a-Si:H capacitor biases. The authors have previously shown that measuring EDMR and MR amplitudes and comparing with calculated energy band diagrams may allow for a rough approximation of defect energy levels in a variety of systems.[14] Unfortunately, the band offsets for the p-Si/a-Si:H and p-Si/a-C:H systems are not well understood. However, the close correspondence between EDMR and MR amplitudes as a function of bias provides strong evidence that the defects responsible for both the EDMR and MR responses are at the same energy levels. Thus, we provide strong circumstantial evidence that silicon dangling bonds are responsible for the near-zero field MR response in a-Si:H and a-C:H systems in this study.
Table 6.1. Summary of EDMR and MR results in this Chapter.

<table>
<thead>
<tr>
<th>System</th>
<th>MR ΔI/I (%)</th>
<th>EDMR ΔI/I (%)</th>
<th>MR Line Width (Gauss)</th>
<th>EDMR Line Width at 350 MHz (Gauss)</th>
<th>EDMR Line Width at 9.5 GHz (Gauss)</th>
<th>Δg</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm a-Si:H</td>
<td>0.05</td>
<td>0.035</td>
<td>17.2</td>
<td>6.1</td>
<td>13</td>
<td>0.0041</td>
</tr>
<tr>
<td>500 nm a-C:H</td>
<td>0.034</td>
<td>0.027</td>
<td>30.8</td>
<td>9.2</td>
<td>11</td>
<td>0.0011</td>
</tr>
<tr>
<td>500 nm a-B:H</td>
<td>0.068</td>
<td>0.003</td>
<td>102</td>
<td>6</td>
<td>12</td>
<td>0.0044</td>
</tr>
<tr>
<td>10 nm a-SiC:H</td>
<td>1.43</td>
<td>1.77</td>
<td>25.2</td>
<td>8.3</td>
<td>10</td>
<td>0.0012</td>
</tr>
<tr>
<td>25 nm p-SiOC:H</td>
<td>0.001</td>
<td>0.00007</td>
<td>7.2</td>
<td>4.8</td>
<td>13</td>
<td>0.0048</td>
</tr>
<tr>
<td>7 nm a-SiCN:H</td>
<td>0.057</td>
<td>0.069</td>
<td>18.1</td>
<td>6.1</td>
<td>14</td>
<td>0.0047</td>
</tr>
</tbody>
</table>
Fig. 6.1. MR and EDMR in a-C:H, a-B:H, a-Si:H, a-SiCN:H, and a-SiC:H. The biases for a-C:H, a-B:H, a-Si:H, a-SiCN:H, and a-SiC:H in this figure are -5 V, 4 V, -1.5 V, -3 V, and -3 V, respectively. Note then in (a), the RF field is off, and no EDMR responses are observed. In (b), the RF field is on at 350 MHz, and EDMR responses are observed in all cases.
Fig. 6.2. MR and EDMR $\Delta I/I$ responses as a function of capacitor bias in Ti/a-Si:H/p-Si structures.
Fig. 6.3. MR and EDMR $\Delta I/I$ responses as a function of capacitor bias in Ti/a-C:H/p-Si structures.
The authors’ previous multiple frequency EDMR studies of a-SiCN:H films indicate that silicon dangling bonds are primarily responsible for SDTAT transport in a-SiCN:H films.[15] Variable bias EDMR measurements in these systems, previously performed at X-band, indicate that the silicon dangling bond centers are near the upper middle part of the a-SiCN:H band gap. A comparison between MR and low-frequency (350 MHz) EDMR measurements is shown in Fig. 6.4. A close correspondence between EDMR and MR amplitudes as a function of bias in a-SiCN:H films is observed. Again, this close correspondence between MR and EDMR amplitudes suggests a common physical connection. Thus, it is likely that both the EDMR and MR responses are due to SDTAT events through silicon dangling bonds in the a-SiCN:H.

We also observe MR phenomena in 25 nm p-SiOC:H films, as shown in Fig. 6.5, with (blue) and without (orange) the applied RF field at 150 MHz. For the a-SiOC:H sample, measurements were taken at 400 K, and at a bias of -3.6 V. The DC current at this temperature is 2.2 mA. The MR and EDMR response amplitudes were 22 nA and 1.5 nA, respectively. The EDMR ΔI/I response amplitude, 0.00068%, is significantly smaller than any other systems analyzed in this chapter. This makes an analysis of ΔI/I versus bias very difficult. Another notable difference between the MR and EDMR responses in the p-SiOC:H system is the phase difference. That is, the net current change is negative for the EDMR response and positive for the MR response. These results jointly suggest that the MR and EDMR responses in the p-SiOC:H system may be of different origin, in contrast with the previous systems.
Figure 6.4. Variable bias EDMR and MR in a-SiCN:H.
Figure 6.5. EDMR and MR spectra in porous a-SiOC:H. Here, the applied bias is -3.6 V, and the temperature is 400 K.
6.4 Summary

We observe MR responses in a-Si:H, a-C:H, a-SiC:H, a-B:H, a-SiOC:H, and a-SiCN:H systems. In most cases, EDMR and MR response amplitudes are comparable, but respective EDMR and MR line widths vary by a factor of 2 or more. We also find no correlation between measured Δg values and zero-field line widths, in agreement with previous suggestions[5-7] that local hyperfine interactions dominate zero-field MR line widths, rather than spin-orbit coupling. We utilize comparisons of EDMR and MR measurement amplitudes to connect defect energy levels to MR phenomena in a-Si:H, a-C:H, and a-SiCN:H systems. Though circumstantial, our findings provide strong evidence that defects responsible for EDMR phenomena are also responsible for MR phenomena in these systems. This simple approach to may be of great use for understanding MR phenomena in a variety of systems outside the scope of this work.
6.5 References


Chapter 7

CONCLUSIONS

In this work, we have utilized magnetic resonance measurements to analyze atomic-scale defects associated with SDTAT currents in a variety of amorphous dielectrics and semiconductors. Additionally, we have utilized EDMR measurements to understand near-zero field MR phenomena in these amorphous dielectrics and semiconductors.

Chapter 4 presented an analysis of a variety of low-κ ILD and CCL materials with both conventional EPR and newly developed EDMR-based approaches. EPR measurements indicate the presence of a variety of dangling bond defects. Though we cannot identify the nature of these defects with conventional EPR alone, we can confirm that remote hydrogen plasma treatments decrease defect density by two orders of magnitude. Also, UV treatments, which are utilized to remove sacrificial porogens in p-SiOC:H, increase defect density by two orders magnitude. To better understand the chemistry of defects in these systems, we utilize multiple frequency EDMR measurements. We first provided baseline measurements of the breadth of $g$ tensor components, $\Delta g$, for silicon and carbon dangling bonds via multiple frequency EDMR measurements in a-Si:H and a-C:H films, respectively. In d-SiOC:H, we find that carbon dangling bonds dominate transport in two d-SiOC:H films with different compositions. In p-SiOC:H films, we find that carbon dangling bonds dominate SDTAT/EDMR prior to porogen removal. However, after porogen removal, multiple frequency EDMR measurements indicate that the dominating defect centers responsible for trap-assisted tunneling currents in these films are silicon dangling bonds. The EDMR and EPR results in p-SiOC:H films jointly indicate that silicon dangling bonds are created by UV treatments. In a-SiNC:H, multiple frequency
EDMR measurements indicate that silicon dangling bonds are primarily responsible for SDTAT in these systems.

To understand defect energy levels in these systems, we utilize multiple bias EDMR measurements. However, since band diagrams have not yet been developed, we utilize a suite of materials to first understand energy band gap and band offsets of the low-κ stacks. A variety of low-κ band gaps were measured via REELS, and band offsets were provided via XPS measurements. By comparing EDMR amplitudes with calculated band diagrams, we can get a rough measure of defect energy levels in these systems. In d-SiOC:H ILDs, we find that carbon dangling bonds, provisionally identified via multiple frequency EDMR, are near the middle of the d-SiOC:H band gap. For d-SiCN:H CCLs, we find that silicon dangling bond centers, again provisionally identified via multiple frequency EDMR, are in the upper part of the d-SiCN:H band gap.

In Chapter 5, we analyze trap-assisted tunneling currents in a-SiN:H via EDMR and MR techniques. We confirm, via multiple frequency EDMR, that K centers dominate transport in a-SiN:H systems, as previously suggested, but not proven. Additionally, we provide K center energy levels via variable bias EDMR measurements. It is found that the K center energy levels are approximately 3.1 eV above the valence band edge. A MR response of comparable amplitude to the EDMR response is detected in the a-SiN:H films. A comparison of EDMR and MR amplitudes versus bias provides strong circumstantial evidence that SDTAT through K centers is responsible for the detection of the MR response in the a-SiN:H films.

In Chapter 6, we observe a ubiquitous nature of MR phenomena in a variety of amorphous dielectrics and semiconductors. MR responses were observed in a-Si:H, a-C:H,
a-SiC:H, a-B:H, a-SiOC:H, and a-SiCN:H. In most cases, EDMR and MR amplitudes are comparable. However, EDMR and MR line widths typically vary by a factor of 2 or more. No correlation was found between measured Δg values and zero-field line widths, suggesting that hyperfine interactions dominate near-zero field MR line width. Similarly to our previous measurements in a-SiN:H, we compare EDMR and MR amplitudes to provide strong circumstantial evidence that defects identified via multiple frequency EDMR are also responsible for MR in these systems. Additionally, we provide a novel method which may be of future utility for understanding MR phenomena in a variety of systems.
NON-TECHNICAL ABSTRACT

Over the past few decades, our society has witnessed an extraordinary growth in technology, which has undoubtedly relied heavily upon the development of modern microelectronics. Applications of microelectronics have had an unprecedented global impact on both the economy, and our quality of life. The level of complexity of modern electronics is a result of decades of multifaceted research and engineering, which requires the collaboration of an array of scientific backgrounds. The birth of microelectronics was fueled by the invention of the transistor; a three-terminal semiconductor device used for an array of applications. Shortly thereafter, the metal-oxide-semiconductor field-effect transistor (MOSFET) was developed. The MOSFET allows for an electrical current to be passed through the transistor when an appropriate voltage is applied to the metal gate. This current may be suppressed by removing the voltage of the metal gate. This voltage-controlled current is the foundation by which modern logic (i.e., an output of ‘0’ or ‘1’) functions. An array of MOSFET devices on one electronic ‘chip’ is called an integrated circuit (IC). ICs are the foundation of a variety of applications including microprocessors, flash drives, flat panel displays, solar cells, and several others. To improve the performance of these ICs, MOSFET and other electronic device dimensions have been scaled down significantly. However, the scaling of MOSFETs over the past several decades has led to several fundamental reliability and performance issues, which become increasingly complicated as MOSFET dimensions approach the atomic scale. Two primary reliability and performance issues which are analyzed in this work involve unwanted electronic leakage, and atomic scale defects.
The materials studied in this work are inherently complex, but crucial to meet the demands of state-of-the-art and next-generation electronic technologies. Unfortunately, the complexity of the systems analyzed in this work makes conventional characterization techniques difficult to utilize. Thus, this work presents a variety of non-conventional magnetic resonance-based techniques which may be used to analyze these complex systems. Additionally, some traditional electronic materials are analyzed in this work as a proof-of-concept of the proposed techniques. The developed techniques rely upon the manipulation of the electron ‘spin,’ which is an intrinsic magnetic field exhibited by every electron. In this study, we analyze the nature by which the electron spins travel through atomic-scale defects. The general field of study of this phenomenon is referred to as spin-transport. We show that these spin-transport-based magnetic resonance techniques may be used to analyze complex material systems when conventional techniques are not entirely useful.

The latter part of this work analyzes a spin-transport based phenomenon called magnetoresistance (MR). That is, if the electrical resistance of a material depends upon the magnitude of an externally applied magnetic field, MR phenomena may be observed. This phenomenon is of interest for various electronic materials applications including spin-quantum computation, which may eventually replace traditional logic-based applications. Unfortunately, MR phenomena are not well understood. In this work, we utilize newly developed magnetic resonance-based techniques to contribute to the understanding of spin-transport-based MR phenomena.
VITA

Mike was born and raised in Westfield, NY. He spent two years studying at Penn State Behrend before transferring to Pennsylvania State University in 2011, where he finished his Bachelor’s in Science with honors in Engineering Science, and a minor in Nanotechnology in 2012. During his undergraduate studies, Mike earned the Scholarship for Talented Students from 2009-2011, and the Mary and Swed Lincoln Scholarship. In January, 2013, he began pursuing a Ph.D. in Materials Science and Engineering at Pennsylvania State University, University Park. Mike’s Ph.D. research, funded by Intel Corporation, involved the development of non-conventional magnetic resonance techniques for understanding atomic scale defects and quantum transport phenomena in amorphous (highly disordered) electronic materials systems. In 2014, Mike was granted the Young Scientist Award courtesy of the Materials Research Society. During his time at Penn State, Mike has first- and co-authored six peer-reviewed journal articles, and has delivered almost 20 oral presentations at scientific conferences across the U.S. and in Europe.

EDUCATION

Pennsylvania State University, University Park, PA
Ph.D. in Materials Science and Engineering, expected December 2016, defending September 2016

- Thesis: Non-Conventional Magnetic Resonance and Magnetoresistance for the Understanding of Defect Chemistry and Spin-Transport Phenomena in Amorphous Dielectrics and Semiconductors
- Advisor: Patrick M. Lenahan, Distinguished Professor of Engineering Science and Mechanics

Pennsylvania State University, University Park, PA
Bachelor of Science in Engineering Science with Honors in Engineering Science
Minor in Nanotechnology

SELECTED PUBLICATIONS

