SAND2022-8393J

Probing the Atomic-Scale Mechanisms of Time-Dependent Dielectric Breakdown in Si/SiO_2 MOSFETs (June 2022)

Fedor V. Sharov, *Student Member, IEEE,* Stephen J. Moxim, *Student Member, IEEE,* Gaddi S. Haase, *Member, IEEE,* David R. Hughart, *Member, IEEE*, Colin. G. McKay, *Member, IEEE,* and Patrick M. Lenahan, *Fellow, IEEE.*

***Abstract*— We report on an atomic-scale study of trap generation in the initial/intermediate stages of time-dependent dielectric breakdown (TDDB) in high-field stressed (100) Si/SiO_2 MOSFETs using two powerful analytical techniques: electrically detected magnetic resonance (EDMR) and near-zero-field magnetoresistance (NZFMR). We find the dominant EDMR-sensitive traps generated throughout the majority of the TDDB process to be silicon dangling bonds at the (100) Si/SiO_2 interface (P_{b0} and P_{b1} centers) for both the spin-dependent recombination (SDR) and trap-assisted tunneling (SDTAT) processes. We find this generation to be linked to both changes in the calculated interface state densities as well as changes in the NZFMR spectra for recombination events at the interface, indicating a redistribution of mobile magnetic nuclei which we conclude could only be due to the redistribution of hydrogen at the interface. Additionally, we observe the generation of traps known as E' centers in EDMR measurements at lower experimental temperatures via SDR measurements at the interface. Our work strongly suggests the involvement of a rate-limiting step in the tunneling process between the silicon dangling bonds generated at the interface and the ones generated throughout the oxide.**

Index Terms*— *EDMR, electrical stressing, interface traps, MOSFETS, silicon dioxide, SDR, SDTAT.

I. Introduction

Time-dependent dielectric breakdown (TDDB) is one of the most important reliability problems in solid-state electronics[1]–[8]. Accelerated reliability tests—such as high constant-voltage stressing and voltage ramping—are routinely used to investigate aging of metal-oxide-semiconductor (MOS) oxides through statistical analysis of oxide breakdown conditions. Such tests can provide considerable insight regarding lifetime prediction. However, without a fundamental atomic understanding of the phenomena involved, the extrapolation of accelerated reliability tests is subject to error. In the work contained herein we hope to contribute to such fundamental understanding.

A. Time-Dependent Dielectric Breakdown

Gate oxide failure in Si/SiO_2 MOSFETs is of great interest in very large-scale integration (VLSI) due to increasing device densities and computational demands of modern integrated circuits. To the extent that there is fundamental physical understanding of TDDB, it is largely due to the result of purely 'electronic' measurements. This relationship between the magnitude of applied gate voltage and the mean breakdown times is well summarized by Berman [1]. As device structures age, their electrical characteristics will change as the quality of their gate oxides degrade. The rate at which this degradation occurs, however, can vary between the scale of seconds to weeks within a range of just a few volts of applied gate bias. High-field stressing involves the application of a gate bias that results in a mean time-to-failure that is observable on a time-scale that is considered to be 'reasonable' for a laboratory measurement.

It is well established that as an MOS oxide is damaged throughout high-field stressing, charge is trapped near the device interface and the density of traps increases, resulting in a decrease in Fowler-Nordheim tunneling currents [8]. As the density of oxide traps increases, trap-assisted tunneling events can become more common, resulting in stress-induced leakage currents (SILC) [4]. But while there is an extensive literature dealing with the purely electronic aspects of these phenomena in high-field stressed Si/SiO_2, the atomic-scale physical and chemical phenomena for TDDB in oxides is not yet fully understood.

Manuscript received June 6th, 2022. This work was supported in part by the U.S. Department of Commerce un Sandia National Laboratories (SNL) is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This work was also supported in part by the Defense Threat Reduction Agency (DTRA) under Award No. HDTRA1-18-0012. The content of the information does not necessarily reflect the position or the policy of the federal government and no official endorsement should be inferred.

F. V. Sharov, S. J. Moxim, and P. M. Lenahan are with the Department of Engineering Science and Mechanics, Pennsylvania State University, State College, PA, 16802 USA (e-mail fvs123@psu.edu).

G. S. Haase, D. R. Hughart, and C. G. McKay are with Sandia National Laboratories, Albequerque, NM 871234 USA.

II. Magnetic Resonance

A. Background on Si/SiO2 Reliability Defects

Magnetic resonance [9] is a powerful spectroscopic tool with unrivaled analytical power for the identification of atomic-scale defects in semiconductors and insulators. As early as the 1970s, conventional electron paramagnetic resonance (EPR) studies began to provide insight into the chemical nature and performance-limiting effects of intrinsic defects in SiO_2 [10], [11]. Since then, a fairly sophisticated understanding of some aspects of reliability physics and defects has been developed as increasingly powerful and sensitive EPR technology have been applied to this system [12]-[25].

Nishi et al. [10] first used this technique to discover intrinsic silicon dangling bond defects at the interface of (111) Si/SiO_2 known as P_b centers: trivalent silicons back bonded to three silicon atoms. Later, two separate P_b centers were identified in the more technologically relevant (100) Si/SiO_2 system. These centers are known as the P_{b0} and P_{b1} defects [11]. The P_{b1} and P_{b0} centers are similar but differ in the details of back-bonding, which leads to different EPR g-tensors and a difference in symmetry.

Other relevant defects in Si/SiO_2 are the oxide traps known as E' centers [12]–[15]. The E' center is also a silicon dangling bond, however, its central silicon is back bonded to three oxygens. While these centers are most often concentrated near the interface, they are not necessarily limited to any one location within the oxide and have been previously associated with trap-to-trap tunneling events within gate oxides [3],[16],[17]. Much of the early EPR investigation of the reliability of Si/SiO_2 dealt with radiation damage [12]-[15],[18], but there were investigations into the electrical reliability of these films as well. These early studies demonstrated important roles for the E' centers. Warren et al. compared the effects of high-field stressing with that of radiation damage in (111) Si/SiO_2 films [18]. In their work, Warren et al. found the generation of large concentrations of E' centers in their oxides as a result of high electric field corona biasing, which could be subsequently annihilated via photo-injection, followed by the formation of a P_b center response [19]. Warren's results were consistent with the population of paramagnetic P_b centers being a strong function of the Fermi level with respect to the interface band-gap (the P_b centers have two levels broadly distributed in the band-gap of silicon [12], [20], [23]) and the fact that many of the E' centers are positively charged.

As positive charge enters the oxide at E' centers and possibly other sites through stressing, the Si/SiO_2 interface Fermi level would move closer to the conduction-band edge. Conversely, as negative charge enters the oxide during the ultra-violet irradiation, the photo injection reduces the net positive charge in the oxide and the Fermi energy moves closer to mid-gap as the positively charged E' centers are rendered neutral by electrons. This in turn results in an increase in the fraction of neutrally charged paramagnetic P_b centers.

A more complex switching behavior of E' centers, also called border traps, has been well-documented in literature [13],[24],[25], in large part due to the analytical power provided by EPR. Further investigation into the effect of high-field stressing into the more technologically relevant (100) Si/SiO_2 was never realized in EPR studies of that time; however, the generation of near-interface E' [16] and P_b [17] centers were clearly correlated to increasing leakage currents via the use of irradiation with 10.2 eV vacuum ultra-violet (VUV) photons.

Later, electrically detected magnetic resonance (EDMR) studies of defect generation in high-field stressed device structures provided further insight into TDDB. Stathis et al. correlated EDMR amplitudes with SILC in thin films (albeit without the clear identification of a specific defect) [21], while Ono et al. showed the generation of both P_{b0} and E' centers at the interface of Si/SiO_2 MOSFETs via SDR measurements [22]. Additionally, we have previously shown in SDR measurements of high-field stressed Si/SiO_2 MOSFETs that there is a significant generation of P_{b0} and P_{b1} defects in close proximity of the device interface [26], [27].

B. Electron Paramagnetic Resonance

In this study, we use electrically detected magnetic resonance (EDMR) as well as a new technique called near-zero-field magnetoresistance (NZFMR) to study the degradation of Si/SiO_2 MOSFETs due to high electric field stressing. We pair our results with dc I-V measurements to analyze interface defect densities at various stress times, and investigate the relevant defects involved in gate oxide tunneling and recombination at the Si/SiO_2 interface. To fully understand the EDMR and NZFMR results, a brief introduction on EPR may be useful.

In EPR, a sample containing paramagnetic defects is placed within a resonant cavity inside a large electromagnet. Microwave irradiation with frequency ν is then supplied to the cavity, which is typically tuned to an *X*-band frequency around 9-10 GHz, and an additional pair of modulation coils apply a small-amplitude, audio-frequency magnetic field across the sample. As the magnetic field of the electromagnet is swept through a resonant magnetic field $\boldsymbol{B_r}$, a diode detects differences in reflected microwave power due to the resonance induced spin-state transitions within the sample, resulting in the absorption of the incoming microwave power at resonance.

For the simple case of an electron which otherwise does not interact with its environment, this resonant response is due to the spin-flipping of an otherwise isolated electron. This resonance condition is

$$h\boldsymbol{\nu} = g_e \mu_B \boldsymbol{B_r}. \tag{1}$$

In this expression, μ_B is the Bohr magneton, h is Planck's constant, and g_e is a constant called the Lande g-factor. Here, the EPR response will be given by a line centered at the resonant field $\boldsymbol{B_r}$, which will depend on the experimental microwave frequency $\boldsymbol{\nu}$. However, the electrons residing in defect sites such as E' and P_b centers do interact with their surroundings and thus the resonance conditions are affected by perturbations based on the defect's atomic structure and surroundings. These perturbations give EPR its analytical power. For the defects of relevance to this study, the perturbations can be expressed in the spin Hamiltonian

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

In this expression, $\boldsymbol{g}$ is an orientation dependent value, typically expressed as a second rank tensor which describes the effects of spin orbit coupling. The term $\boldsymbol{S}$ denotes the electron spin. The product $\boldsymbol{A}_i\boldsymbol{I}_i$ describes electron-nuclear hyperfine interactions, where $\boldsymbol{A}_i$ is a second rank tensor and $\boldsymbol{I}_i$ represents the spin on the $\boldsymbol{i}$th nucleus. Conventional EPR has a sensitivity of about 10^{10} total defects [28]. Since there are far fewer than 10^{10} total defects in any even remotely technologically relevant MOS transistors, there was a need for significant improvements in sensitivity to tackle device reliability issues involving various stressing mechanisms in individual devices.

C. Electrically Detected Magnetic Resonance

As mentioned, the sensitivity limitations of conventional EPR limits its analytical power in defect identification in modern Si/SiO_2 MOSFETs. This problem, however, can be addressed through a much more sensitive EPR detection technique called electrically detected magnetic resonance (EDMR). EDMR is, arguably, the most powerful method for identifying the chemical and physical nature of electrical defects in semiconductor devices. EDMR utilizes the same physical principles as conventional EPR in that the defect identification takes place through observation of the effects of spin-orbit coupling and electron-nuclear hyperfine interactions on the magnetic resonance spectra of the defects involved. However, EDMR differs from EPR in its detection scheme; it directly measures spin-dependent phenomena via changes in device current or voltage. EDMR is roughly ten million times more sensitive than conventional EPR; it can detect 1000 or fewer defects in a device structure under study. This increase in sensitivity makes it a powerful tool to explore reliability issues of individual fully processed transistors. A schematic diagram of a high-field EDMR spectrometer is shown in Fig. 1.

We utilize EDMR via two different biasing schemes and spin-dependent detection methods. The first method, spin-dependent trap-assisted tunneling (SDTAT) [29], involves the detection of spin-dependent current through the gate oxide directly. The mechanism of trap-to-trap tunneling or variable range hopping (VRH) [30] involves tunneling events which will depend on the difference in the traps' energies and their physical separation. The possibility of a trap to trap tunneling transition is additionally dependent on the spin states of the tunneling electron and defect site. If both sites involved in the tunneling event are occupied by an unpaired electron, the electron spin states matter. The Pauli exclusion principle will prevent tunneling if both electrons have the same spin quantum number. It is best to envision this process in terms of a pair of electron spins. If both spin quantum numbers are the same, we refer to the pair as a triplet. For the opposite spin cases, we refer to the system as a singlet.

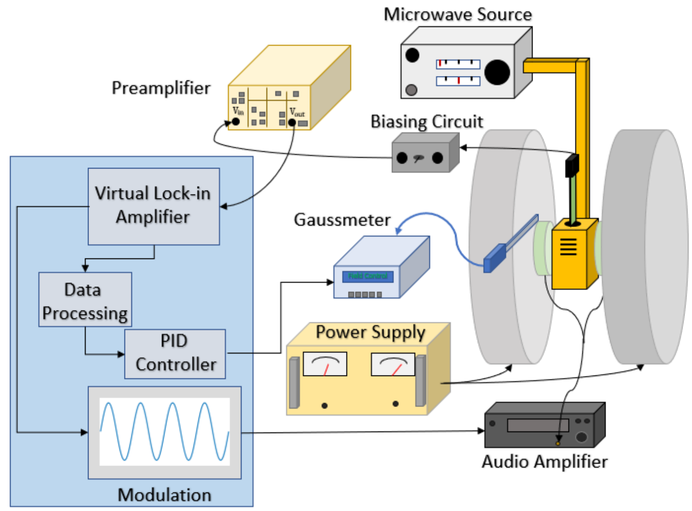

Fig. 1. Schematic diagram of a high-field electrically detected magnetic resonance (EDMR) spectrometer.

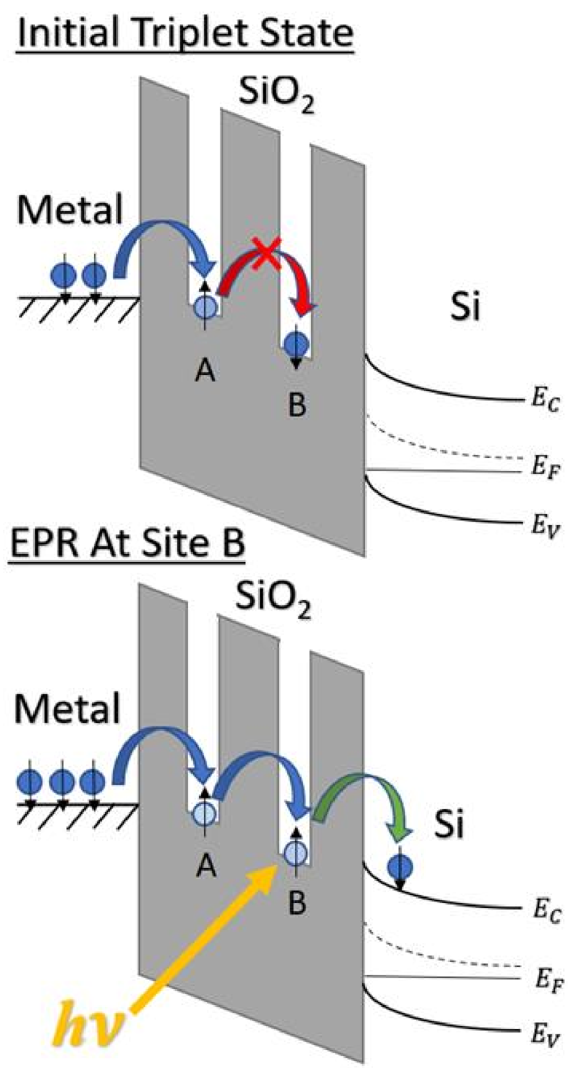

Fig. 2. Schematic diagram of the spin-dependent trap-assisted tunneling (SDTAT) process in an n-channel MOSFET operating in accumulation. Suppose that the pair of spins are in the triplet state at defect A and B. In this case, tunneling is forbidden. At resonance, the spin at defect site B can flip, rendering the tunneling event possible.

Due to the presence of an oscillating microwave field in EDMR, when the magnetic field reaches the resonant condition for the triplet defect sites, the electron spin of one site can 'flip,' creating a singlet pair which will allow the electron tunneling event. This event will change the leakage current, and the identity of relevant tunneling sites can be deduced from the microwave frequency and magnetic field at resonance. A schematic of the SDTAT process is shown in Fig. 2.

Another spin-dependent mechanism used in this study is spin-dependent recombination (SDR) [31], [32]. The Pauli exclusion principle can also be applied to recombination events within a semiconductor system. For example, if a certain deep-level defect is coupled to a nearby conduction electron with the same spin quantum numbers, recombination involving this pair of electrons at the defect site will be forbidden. However, at the resonant condition for the defect, the spin of the deep-level defect can 'flip,' allowing a recombination event between the conduction electron and deep-level defect. Such events result in a measurable change in the recombination current. The detection of SDR in MOSFETs can be observed with various biasing schemes [32].

The biasing scheme used for the SDR measurements in this study is the Fitzgerald-Grove gated diode method, commonly referred to as the dc I-V technique [34]. In the dc I-V approach, the body is held at virtual ground and the source/drain to body diodes are slightly forward biased to inject minority carriers into the channel, while the gate voltage is swept from accumulation to inversion. At a gate voltage at which the interface quasi-Fermi levels are symmetric about the Si interface intrinsic energy, the source/drain to body current will reach a maximum value, corresponding to a maximum recombination of traps at the interface. This peak in the current is given by the expression:

$$\Delta I_{DCIV} = \frac{1}{2} q n_i \sigma v_{th} D_{it} A q |V_f| \exp\left(\frac{q|V_f|}{2k_B T}\right), \quad (3)$$

where D_{it} is the density of traps per unit area near the middle of the silicon band gap at the Si/SiO$_2$ interface as a function of the source/drain forward bias V_f, n_i corresponds to the intrinsic carrier concentration, σ is the geometric mean of the capture cross section for holes and electrons, A is the gate area, and v_{th} is the thermal velocity. The values of q, k_B, and T correspond to the elementary charge, Boltzmann's constant, and absolute temperature, respectively.

Biasing a MOSFET at voltages corresponding to the peak dc I-V current provides a particularly convenient EDMR biasing scheme which can result in a significant SDR response that is exclusively sensitive to defects at or near the device interface. It also allows for the calculation and correlation of EDMR defect amplitudes with calculated defect densities. A schematic for this biasing scheme is shown in Fig. 3.

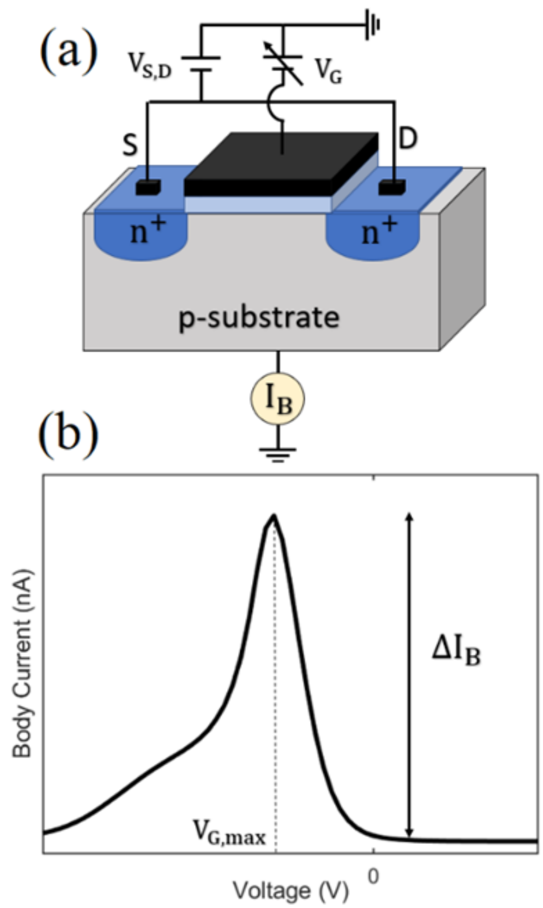

Fig. 3. Schematic diagram of an (a) n-channel MOSFET biased with dc I-V and (b) the resultant body current vs. gate voltage characteristics.

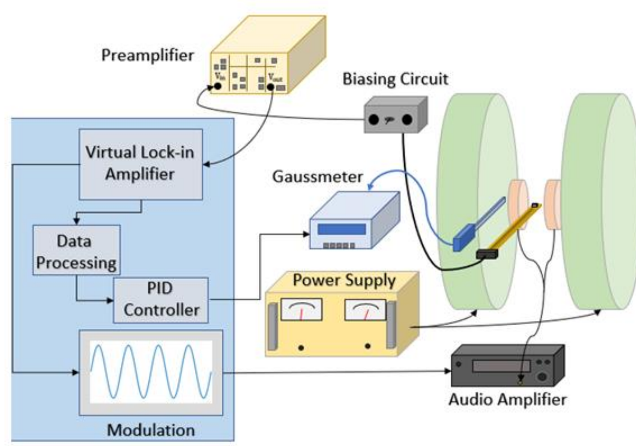

Fig. 4. Schematic diagram of a near-zero-field magnetoresistance (NZFMR) spectrometer.

D. Near-Zero-Field Magnetoresistance

In addition to EDMR, we have another tool at our disposal for the detection of spin-dependent mechanisms called near-zero-field magnetoresistance (NZFMR) [35]–[38]. NZFMR can detect both the SDR and SDTAT phenomena described in the previous section, albeit due to different physical mechanisms. An NZFMR spectrometer is essentially an EDMR spectrometer, except for two things: no microwave source is required and only a small magnetic field is utilized. A schematic of a typical NZFMR spectrometer is shown in Fig. 4.

In our NZFMR measurements, we utilize the mixing of singlet and triplet states of pairs of electrons at near-zero fields. Due to the absence of a substantial external magnetic field, there is no longer a g-value to be gleaned from the spectra; however, the NZFMR spectra provide atomic-scale information on both hyperfine interactions within the system and the kinetic processes involved in both SDR and SDTAT. NZFMR has been successfully modeled through the use of the stochastic quantum Liouville equation (SLE) [35], and this technique has been recently used to extract hyperfine constants in device systems [35].

III. Experimental

The devices used in this study were Si/SiO_2 n-channel MOSFET structures with 7.5 nm thick gate oxides fabricated through a standard industrial process. The MOS structures were sets of 126 individual MOSFETs, each with 15 μm × 1 μm channel dimensions. The devices were chained together to yield strong EDMR and NZFMR signals. High-field stressing was performed at a constant gate bias of -9.0 V for all of the MOSFETs used in this study, corresponding to an average electric field of 12 MV/cm. Between these high-field stressing treatments, devices were electrically characterized via dc I-V measurements prior to being placed into an EDMR/NZFMR spectrometer. Both the stress and dc I-V electrical measurements were made with a Hewlett-Packard 4145A Semiconductor Parameter Analyzer.

To account for any source/drain to body effects throughout stressing and SDTAT, the source, drain, and body terminals of the MOSFETs were shorted together and virtually grounded. The X-band SDTAT measurements were made with a home-built spectrometer which consisted of a 4 inch Varian electromagnet modified for EDMR, a Stanford Research Systems SR 570 low-noise current to voltage preamplifier, and a modified Resonance Instruments Model 8625 X-band microwave bridge. The modulation amplitude and frequency used in these experiments were 0.4 mT and 1 kHz, respectively. The gate bias used for these measurements was -5 V, corresponding to an average gate oxide electrical field of 6.6 MV/cm. Additionally, an adaptive signal averaging filtering algorithm was used to help resolve these measurements [37] due to the low magnitude of leakage current observed within these devices at the gate biasing conditions below the electric breakdown field.

The X-band SDR measurements were made with a similar apparatus which was additionally outfitted with a four terminal biasing box for source/drain, body, and gate control necessary for dc I-V EDMR measurements. Additionally, a Bruker ER 4111 VT IBM Instruments Variable Temperature Unit was utilized in the low-temperature dc I-V EDMR measurements. Temperatures other than room temperature have sometimes been utilized to increase the sensitivity of EDMR measurements to certain defects. The reasoning for this can be complicated; factors can include increasing the spin-lattice relaxation times as well as changes in times involved in electronic transport and/or dwelling times involved in electrical transport [29]. For example, Ono et al. [22] has previously demonstrated that temperature conditions played a significant role in the detection sensitivity of different traps in Si/SiO_2 in SDR using another EDMR technique called spin-dependent charge-pumping. To maximize the signal-to-noise ratio of these measurements, modulation amplitudes of 0.6 mT were used during the variable temperature study.

Once a temperature was found in which all the spectral features appeared, the dc I-V measurements were repeated at a lower modulation amplitude of 0.2 mT, corresponding to the smallest linewidth of the EDMR response (the E' center). All EDMR measurements in this study were made with the magnetic field perpendicular to the (100) interface.

The NZFMR measurements were made on another custom-built low-field spectrometer operating from $\pm$20 mT. Similar to the EDMR measurements, a Stanford preamplifier and modulation frequency of 1 kHz was used throughout all measurements, and a custom-built biasing box was used to maintain the dc I-V conditions for maximum recombination at a source/drain diode bias of -0.33 V. The modulation amplitudes used in the SDTAT and dc I-V NZFMR measurements were 0.4 mT and 0.1 mT, respectively.

IV. Results

A representative example of the leakage current vs. time characteristics throughout the -9 V constant bias high-field stressing for the device used in the X-band SDTAT experiments is shown in Fig. 5, with discontinuities corresponding to the interludes involved in subsequent SDTAT measurements. The MOSFETs would, on average, break down shortly after the one-hour mark at this electric field (12 MV/cm). The SDTAT results for these devices are shown in Fig. 6, with signals corresponding to a zero-crossing of g=2.0050. The SDTAT EDMR measurements on the unstressed devices were below our detection limit. The calculated dc I-V interface trap densities for the various stress conditions vs. EDMR currents are shown in Fig. 7 (these values correspond to the density of states near mid-gap). The SDR spectrum for a high-field stressed device is shown in Fig. 8. Fig. 8 (a) shows the change in the SDR spectra at temperatures ranging from 135-300 K, whereas Fig. 8 (b)

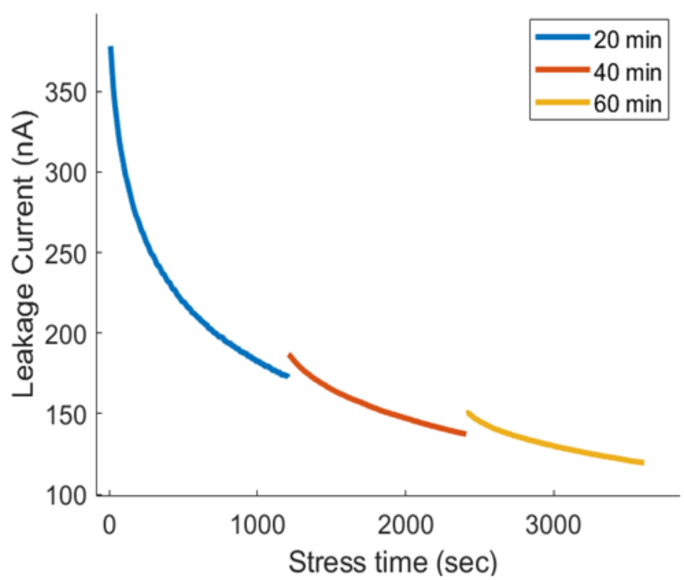

Fig.5. Leakage current characteristics for the Si/SiO_2 MOSFETs stressed at a constant gate bias of – 9 V, corresponding to an average electric field of 12 MV/cm.

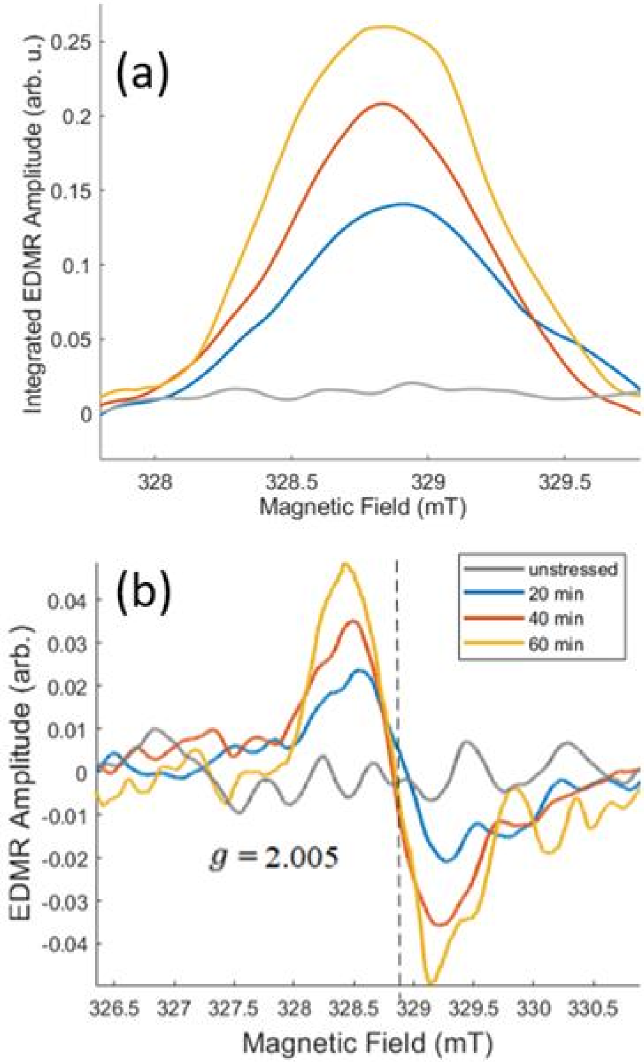

Fig.6. Comparisons of the (a) integrated SDTAT EDMR amplitudes as well as (b) EDMR spectra for the high-field stressed Si/SiO_2 MOSFETs. The zero-crossings in (b) show that the dominating defect are P_b centers (g = 2.005).

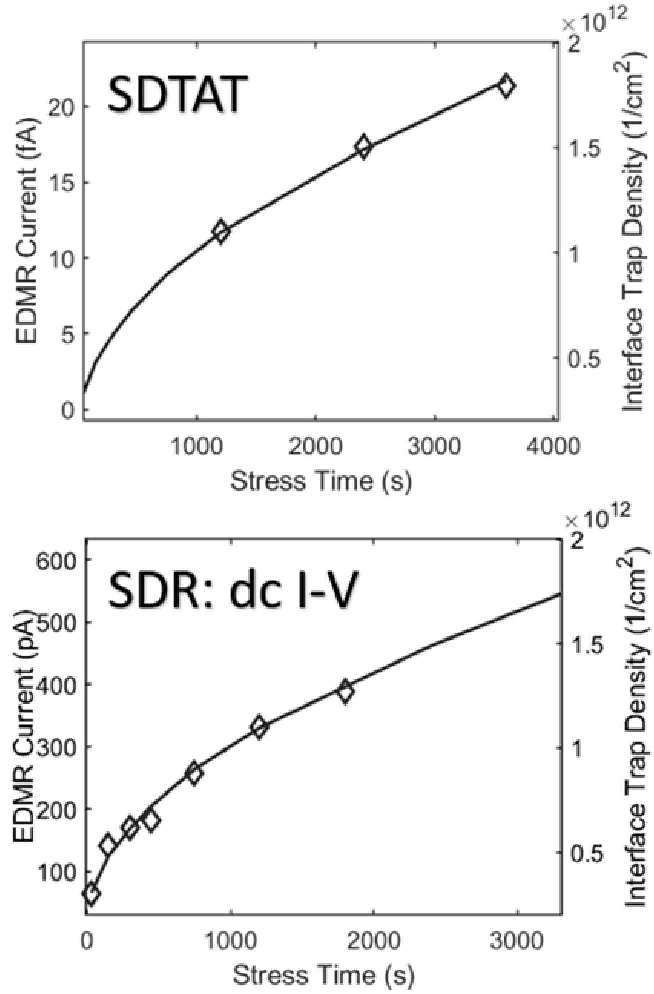

Fig. 7. Comparison of EDMR current change and the interface trap density at various stress times for both the SDTAT (top) and SDR (bottom) measurements.

shows a much more defined and longer-averaged spectra with clear evidence of multiple defect signals. NZFMR dc I-V measurements for a Si/SiO_2 MOSFET at various stress times is shown in Fig. 10. NZFMR SDTAT spectra at various gate biases for a device stressed for an hour at -9 V are shown in Fig. 11.

V. Discussion

The I-V characteristics in Fig. 5 show clear evidence of charge trapping events throughout the case of the -9 V stress. At this gate voltage, the mean breakdown time of these MOSFETs was approximately an hour, so the data points selected evenly throughout the devices lifetime were a representative selection for the traps generated throughout the majority of the TDDB process. Even after the high-field stressing, the gate-oxide current at -5 V remained on the order of $\approx 10^{-10}$ A. Even at these small currents, an SDTAT response with a zero-crossing of g = 2.0050 increases throughout the device lifetime. SDTAT relies on the observation of trap-to-trap tunneling and variable range hopping events, meaning the growth of this signal clearly indicates the detection of newly formed traps during stressing. This is no surprise given the many theories involving trap generation throughout TDDB garnered from spectroscopic [16]-[21] and electrical measurements [1]-[4]. The identity of the traps observed, however, is surprising. With the magnetic field perpendicular to the (100) interface plane, the observed signal is dominated by interface silicon dangling bonds known as P_b centers: the (100) interface P_{b0} center (g = 2.0059) at this field orientation) and a possible P_{b1} center (g = 2.0032 at this orientation) contribution [10], [11]. The EDMR amplitude vs. stress-time results shown in Fig. 7 strongly indicate the amplitude of this response is almost entirely due to the increase in interface trap density, as the results of SDR shown both in this study and elsewhere [23]. As is the case with SDR measurements, the EDMR amplitudes track with interface trap density. There is, however, no clear evidence of a response from the oxide defects known as E' centers.

Previous EPR experiments on high-field stressing of Si/SiO_2 have demonstrated a significant generation of E' centers throughout bulk films [17]-[19]. While these studies were not detecting these defects electrically, and high-voltage stressing used corona-biasing, one would expect that the defects that formed would be similar to those in an SDTAT experiment of high-field stressed Si/SiO_2. One could argue that, due to the known rapid formation of interface dangling bonds throughout high-field stressing as well as the mediocre signal-to-noise ratios of the SDTAT measurements, the response from the E' oxide dangling bond is simply being smothered. However, in an oxide as thick as 7.5 nm, there should be multiple hopping events on the tunneling path across the oxide so an E' response should still be expected in the SDTAT measurement.

The dc I-V measurements in Fig. 8 show the spectra due to defects responsible from recombination events near the Si/SiO_2 interface. At first glance, the room-temperature (300 K) measurements shown in Fig. 8 (a) clearly show a similar response to the SDTAT in Fig. 6 with the P_{b0} and P_{b1} center dominating the spectra. As the temperature is lowered, a new signal emerges at a g=2.000; a response that could only be due to increased sensitivity to the E' oxide dangling bond (g = 2.0007) [14]-[15]. The results in Fig. 8 (b) show a better resolved picture of the defect centers generated by high-field stressing due to the use of a lower modulation amplitude, clearly indicating P_{b0}, P_{b1}, and E' contributions.

It is generally thought that oxide traps generated throughout high-field stressing are broadly distributed and are responsible for increases in trap-to-trap tunneling events observed in stress-induced leakage currents [5]. However, the dc I-V measurement is only sensitive to near mid-gap defects close to the interface. Assuming these oxide traps are spatially distributed more broadly than in the case of gamma irradiation, then the generation of an observable E' response is a very strong argument that E' defects are generated in the oxide. So, why is this response not clear in the SDTAT measurement?

One theory, initially proposed by Frantz et al. [35] in their SDTAT study of Si/SiO_2 capacitor structures, is that the Si/SiO_2 interface to oxide tunneling response acts as a rate-limiting step in the tunneling process. Given the difficulty of observing E' defect spectra in Si/SiO_2 SDTAT in the past, this theory seems to be consistent with the results observed in this study. For example, Moxim et al. [36] previously studied gamma irradiated (100) Si/SiO_2 transistors, a process which surely resulted in a significant generation of E' traps [25], [31]. However, even in those SDTAT measurements, the dominating spectral features were still the P_{b0} and P_{b1} centers. It is clear that there must be some fundamental physical reason why these states are not detected in spin-dependent tunneling measurements. As illustrated in Fig. 9, a plausible explanation could be that tunneling between oxide E' defects and interface P_b centers is the rate limiting step in the tunneling process. If the interface to oxide tunneling process limits the SDTAT, it is likely that these oxide-oxide tunneling events could still be detectable in SDTAT in structures with much larger areas or smaller gate thicknesses, and thus a much larger SDTAT sensitivity.

The dc I-V NZFMR results in Fig. 10 provide further insight into the effects of high-field stressing at the Si/SiO_2 interface. As shown by Moxim et al. [37], NZFMR can, much like EDMR, be used to monitor the formation of traps

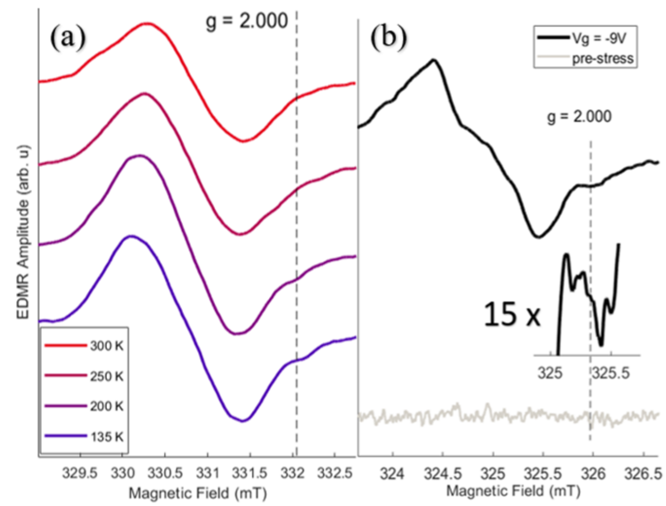

Fig. 8. (a) High modulation amplitude SDR traces of a MOSFET stressed for -9 V for 20 minutes at various decreasing temperature conditions and (b) higher resolution low amplitude modulated SDR EDMR results at 200 K for a pre-stress (bottom) and post-stressed (top) Si/SiO_2 MOSFET with an additional E' center (g = 2.000) response at the interface.

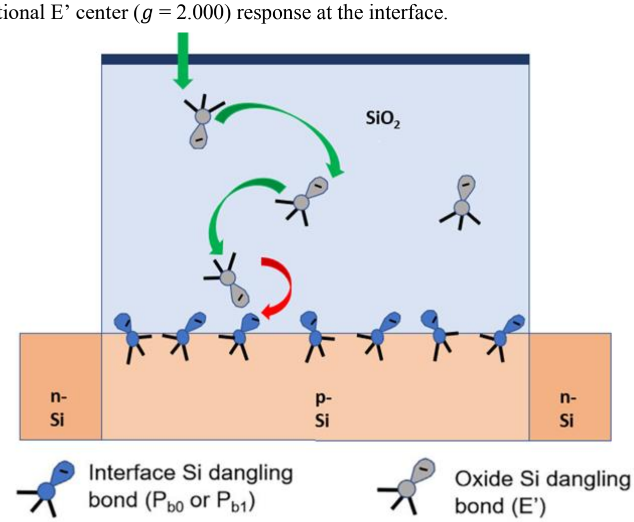

Fig. 9. (a) Atomic-scale schematic for the proposed rate-limiting tunneling event between an E' oxide defect and an interface dangling bond (P_{b0} and P_{b1}) at the (100) interface.

throughout high-field stressing via analysis of NZFMR amplitudes. Additionally, the line shapes of these NZFMR traces have been previously modeled using the stochastic quantum Liouville equation (SLE) [34], [35] via the consideration of electron-nuclei hyperfine coupling constants and kinetics involved with recombination and tunneling processes. By normalizing the amplitudes of these NZFMR responses, one can analyze either changes in these rates involved in electrical processes or changes in the hyperfine interactions in equivalent electrical processes. The dc I-V measurements shown in Fig. 10 deal with identical devices with identical biasing conditions; one would not expect any changes in recombination kinetics between these measurements. Instead, any observed changes in this line shape will be entirely due to changes in hyperfine interactions with mobile magnetic nuclei near the interface.

There are only two potential magnetic nuclei at the Si/SiO_2 interface: the ^{29}Si nuclei (4.7% abundance) and hydrogen

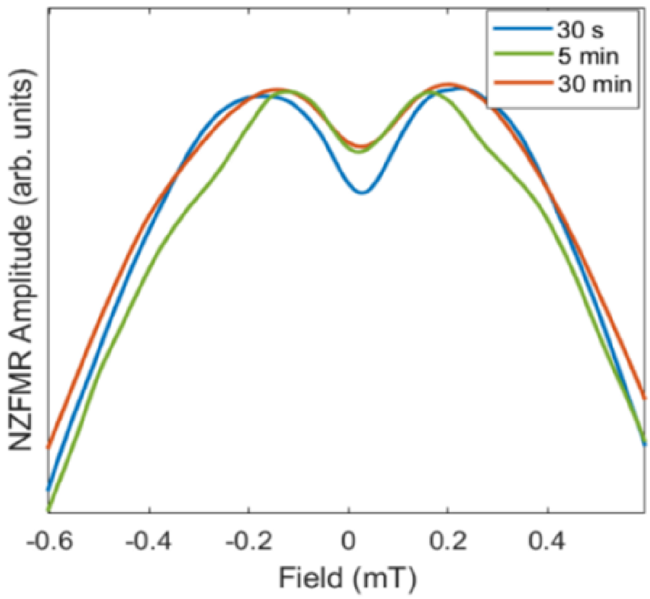

Fig. 10. Comparisons of the integrated NZFR dc I-V response in Si/SiO_2 MOSFETS at -9 V for 30 seconds, 5 minutes, 30 minutes. The changes in the central response are due to changes in the hyperfine interactions near the interface due to the duration of the high-field stress, indicating a redistribution of hydrogen throughout the stress process.

nuclei (100% abundance). Of these two nuclei, only the hydrogen nuclei could be mobile during high-field stressing. The importance of hydrogen motion has been argued to be important throughout the TDDB process [5]-[7]. These results provide direct evidence that NZFMR can track hydrogen redistribution at and around the Si/SiO_2 interface.

Fig. 11 shows another trend that can be detected in NZFMR: the effect of gate bias on an Si/SiO_2 MOSFET which has been significantly high-field stressed at -9 V for an hour. In this case, most of the relevant defect generation occurs rapidly at the early stages of high-field stressing [8], [23]. The comparatively low voltage (-2 to -5 V) SDTAT measurements used in generating the spectra in Fig. 11 are not expected to meaningfully alter the defect concentrations on the scale of the measurement time. Instead, they show dramatic changes in the line shapes that indicate significant changes in the tunneling rates involved in the SDTAT process. Unfortunately, the formation of percolation paths throughout the TDDB process can both serve to change tunneling rates and as well as hyperfine interactions, making quantitative analysis of the NZFMR SDTAT spectra difficult. Nevertheless, it is clear that these spectra contain information about the defects involved in the trap-assisted tunneling process.

While both trends in Fig. 10 and Fig. 11 are modellable via the SLE, the practical execution of fitting these trends are currently limited by the complexity of the defect forming process defects in high-field stressing of (100) Si/SiO_2. To further study these effects, it would be useful to repeat these experiments on (111) Si/SiO_2 interfaces, for which only one P_b variant exists [10]. Simplifying the system would help to glean meaningful information about the kinetics of trap-to-trap tunneling and ascertain the role of hydrogen in the TDDB process.

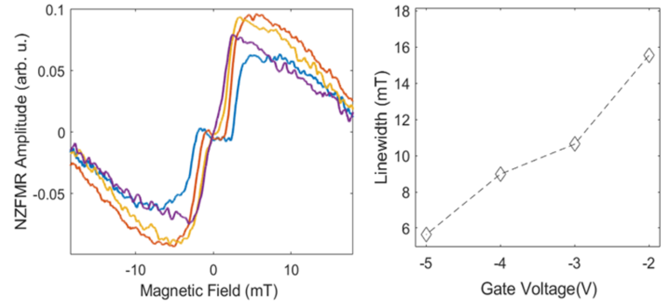

Fig. 11. Comparisons of NZFMR SDTAT in Si/SiO_2 MOSFETs stressed at –9 V for 60 minutes at various gate biases. The significant change in linewidths (5-16 mT) is due in part from band-bending in the MOS kinetics of the trap-assisted tunneling process.

VI. Conclusion

We investigated the role of the atomic-scale traps involved in TDDB in (100) Si/SiO_2 MOSFETs and found EDMR evidence of significant trap generation throughout high-field stressing. Specifically, we find that the (100) Si/SiO_2 silicon dangling bonds, i.e., the P_{b0} and P_{b1} centers, to be the dominant trap in both the SDTAT and SDR EDMR spectra. We find the amplitudes of the spin-dependent current for both defects to be consistent with the calculated interface densities throughout the early and intermediate stages of TDDB.

Additionally, we find a temperature-dependent EDMR response of near-interface oxide dangling bonds known as E' centers in our SDR measurements generated by high-field stressing. We conclude that while E' centers are undoubtedly being generated throughout high-field stressing, there must be a significant enough difference between the rates of oxide trap-to-oxide trap tunneling events and interface-to-oxide tunneling events. We propose that interface-to-oxide tunneling events act as the rate-limiting step. We recommend additional investigation via both larger area devices or different gate oxide thicknesses, as well as investigation into the variation of these traps' energy levels via external stimuli and/or temperature.

Furthermore, we present data on NZFMR—a relatively new technique that can be used on packaged devices—that indicate the measurement may provide valuable information about TDDB mechanisms. Most notably, our data shows that the measurement could be used to monitor the motion of hydrogen at the Si/SiO_2 interface throughout high-field stressing; we suggest that this trend would more easily be understood in the simpler system of (111) Si/SiO_2. We also find significant differences in the NZFMR spectra of SDTAT as a function of gate bias; these differences could be used to better understand the kinetics and role of different traps in both trap-to-trap tunneling throughout the TDDB process.

Acknowledgment

Sandia National Laboratories (SNL) is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

This work was also supported in part by the Defense Threat Reduction Agency (DTRA) under Award No. HDTRA1-18-0012. The content of the information does not necessarily reflect the position or the policy of the federal government and no official endorsement should be inferred.

REFERENCES

[1] A. Berman, "Time-Zero Dielectric Reliability Test By a Ramp Method.," *Annu. Proc. - Reliab. Phys.*, pp. 204–209, Apr. 1981.

[2] D. J. DiMaria and J. H. Stathis, "Anode hole injection, defect generation, and breakdown in ultrathin silicon dioxide films," *J. Appl. Phys.*, vol. 89, no. 9, pp. 5015–5024, May 2001.

[3] J. W. Mcpherson, *Reliability Physics and Engineering: Time-to-failure modeling*. New York: Springer, 2013.

[4] J. De Blauwe, J. Van Houdt, D. Wellekens, G. Groeseneken, and H. E. Macs, "SILC-related effects in flash e2PROM's-Part I: A Quantitative model for steady-state SILC," *IEEE Trans. Electron Devices*, vol. 45, no. 8, pp. 1745–1750, Aug. 1998.

[5] P. E. Blochl, "First-principles calculations of defects in oxygen-deficient silica exposed to hydrogen," *Phys. Rev. B.,* pp. 6158-6179, vol. 62, no. 10, Sep. 2000.

[6] D. J. DiMaria, E. Cartier, and D. Arnold, "Impact ionization, trap creation, degradation, and breakdown in silicon dioxide films on silicon," *J. Appl. Phys.,* vol. 73, no. 7, pp. 3367-3383, Jun. 1998.

[7] J. Tahir-Kheli, M. Miyata, W. A. Goddard III, "Dielectric breakdown in SiO_2 via elecric field induced attach hydrogen defects," *Microelectron. Eng.*, vol. 80, pp. 174-177, Jun. 2005.

[8] C. Zener, "A theory of electrical breakdown of solid dielectrics," *Proc. R. Soc. London Ser. A*, vol. 143, pp. 523–529, Jul. 1934.

[9] J. . Weil, J.H., Bolton, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*. New York, 1994.

[10] Y. Nishi, K. Tanaka, and A. Ohwada, "Study of silicon-silicon dioxide structure by electron spin resonance II," *Jpn. J. Appl. Phys.*, vol. 11, no. 1, pp. 85–91, Jan. 1972.

[11] P. J. Caplan, E. H. Poindexter, B. E. Deal, and R. R. Razouk, "ESR centers, interface states, and oxide fixed charge in thermally oxidized silicon wafers," *J. Appl. Phys.*, vol. 50, no. 9, pp. 5847–5854, Sep. 1979.

[12] P. M. Lenahan and P. V. Dressendorfer, "Hole traps and trivalent silicon centers in metal/oxide/silicon devices," *J. Appl. Phys.*, vol. 55, no. 10, pp. 3495–3499, May 1984.

[13] J. F. Conley, P. M. Lenahan, A. J. Lelis, and T. R. Oldham, "Electron spin resonance evidence that E′γ centers can behave as switching oxide traps," *IEEE Trans. Nucl. Sci.*, vol. 42, no. 6, pp. 1744–1749, Dec. 1995.

[14] L. Lipkin, L. Rowan, A. Reisman, and C. K. Williams, "Correlation of Fixed Positive Charge and E′γ Centers as Measured via Electron Injection and Electron Paramagnetic Resonance Techniques," *J. Electrochem. Soc.*, vol. 138, no. 7, pp. 2050–2052, Jul. 1991.

[15] P. M. Lenahan and P. V. Dressendorfer, "Microstructural Variations in Radiation Hard and Soft Oxides Observed through Electron Spin Resonance," *IEEE Trans. Nucl. Sci.*, vol. 30, no. 6, Dec. 1983.

[16] P. M. Lenahan, J. J. Mele, R. K. Lowry, and D. Woodbury, "Leakage currents and silicon dangling bonds in amorphous silicon dioxide thin films," *J. Non. Cryst. Solids*, vol. 266-269 B, pp. 835–839, May 2000.

[17] P. M. Lenahan *et al.*, "Direct experimental evidence linking silicon dangling bond defects to oxide leakage currents," *IEEE Int. Reliab. Phys. Symp. Proc.*, vol. 2001, pp. 150–155, Apr. 2001.

[18] W. L. Warren and P. M. Lenahan, "A comparison of positive charge generation in high field stressing and ionizing radiation on mos structures," *IEEE Trans. Nucl. Sci.*, vol. 34, no. 6, pp. 1355–1358, Dec. 1987.

[19] W. L. Warren and P. M. Lenahan, "Electron spin resonance study of high field stressing in metal-oxide-silicon device oxides," *Appl. Phys. Lett.*, vol. 49, no. 19, pp. 1296–1298, Nov. 1986.

[20] P. M. Lenahan and J. R. Conley, "A comprehensive physically based predictive model for radiation damage in MOS systems," *IEEE Trans. Nucl. Sci.*, vol. 45, no. 6, pp. 2413–2423, Dec. 1998.

[21] J. H. Stathis, "Electrically detected magnetic resonance study of stress-induced leakage current in thin SiO_2," *Appl. Phys. Lett.*, vol. 68, no. 12, pp. 1669–1671, Mar. 1996.

[22] M. Hori and Y. Ono, "Charge Pumping under Spin Resonance in Si (100) Metal-Oxide-Semiconductor Transistors," *Phys. Rev. Appl.*, vol. 11, no. 6, Apr. 2019.

[23] P. M. Lenahan and P. V. Dressendorfer, "Effect of bias on radiation-induced paramagnetic defects at the silicon-silicon dioxide interface," *Appl. Phys. Lett.*, vol. 41, no. 6, pp. 542–544, Jun. 1982.

[24] A. J. Lelis and T. R. Oldham, "Time Dependence of Switching Oxide Traps," *IEEE Trans. Nucl. Sci.*, vol. 41, no. 6, pp. 1835–1843, Dec. 1994.

[25] D. M. Fleetwood, "'Border traps' in MOS devices," *IEEE Trans. Nucl. Sci.*, vol. 39, no. 2, pp. 269–271, Apr. 1992.

[26] S. J. Moxim, F. V. Sharov, D. R. Hughart, G. S. Haase, C. G. McKay, and P. M. Lenahan, " Atomic-scale defects generated in the early/intermediate stages of dielectric breakdown in Si/SiO_2 transistors," *Appl. Phys. Lett.*, vol. 120, no. 6, p. 063502, Feb. 2022.

[27] F. V. Sharov, S. J. Moxim, P. M. Lenahan, D. R. Hughart, G. S. Haase, and C. G. McKay, "Understanding the Initial Stages of Time Dependent Dielectric Breakdown in Si/SiO2 MOSFETS Utilizing EDMR and NZFMR," *2021 IEEE International Reliability Workshop (IIRW),* 2021, pp. 1-5.

[28] G. R. Eaton, S. S. Eaton, and K. Ohno, EPR Imaging and in vivo EPR: Sensitivity in EPR imaging, Boca Raton, Florida: CRC Press, 2018, pp. 162-166.

[29] M. A. Anders, P. M. Lenahan, C. J. Cochrane, and J. Van Tol, "Physical nature of electrically detected magnetic resonance through spin dependent trap assisted tunneling in insulators," *J. Appl. Phys.*, vol. 124, no. 21, Dec. 2018.

[30] N. F. Mott, "Conduction in non-crystalline materials," *Philos. Mag. A J. Theor. Exp. Appl. Phys.*, vol. 19, no. 160, pp. 835–852, Apr. 1969.

[31] P. M. Lenahan and M. A. Jupina, "Spin dependent recombination at the silicon/silicon dioxide interface," *Colloids and Surfaces*, vol. 45, no. C, pp. 191–211, 1990.

[32] D. Kaplan, I. Solomon, and N. F. Mott, "Explanation of the large spin-dependent recombination effect in semiconductors," J. Phys. Lett., vol. 39, no. 4, pp. 51–54, Feb. 1978.

[33] D. J. Fitzgerald and A. S. Grove, "Surface Recombination in Semiconductors," *IEEE Trans. Electron Devices*, vol. 15, no. 6, p. 426, 1968.

[34] N. J. Harmon, J. P. Ashton, P. M. Lenahan, and M. E. Flatté, "Near-Zero-Field Spin-Dependent Recombination Current and Electrically Detected Magnetic Resonance from the Si/SiO_2 interface," pp. 1–16, 2020.

[35] E. B. Frantz *et al.*, "Electrically detected magnetic resonance and near-zero field magnetoresistance in 28Si/28SiO2," *J. Appl. Phys.*, vol. 130, no. 6, Aug. 2021.

[36] S. J. Moxim, J. P. Ashton, P. M. Lenahan, M. E. Flatte, N. J. Harmon, and S. W. King, "Observation of Radiation-Induced Leakage Current Defects in MOS Oxides with Multifrequency Electrically Detected Magnetic Resonance and Near-Zero-Field Magnetoresistance," *IEEE Trans. Nucl. Sci.*, vol. 67, no. 1, pp. 228–233, Jan. 2020.

[37] S. J. Moxim, F. V. Sharov, D. R. Hughart, G. S. Haase, C. G. McKay, E. B. Frantz, P. M. Lenahan, "Tracking Atomic-Scale Defects involved in Metal-Oxide-Semiconductor Devices with Simple Near-Zero-Field Magnetoresistance Measurement," *Rev. Sci. Instrum.*, (Submitted) 2022.

[38] B. R. Manning, C. J. Cochrane, and P. M. Lenahan, "An improved adaptive signal averaging technique for noise reduction and tracking enhancements in continuous wave magnetic resonance," *Rev. Sci. Instrum.*, vol. 91, no. 3, Mar. 2020.

Fedor Sharov (Student Member, IEEE) received his B.A.Sc. in Engineering Science and Mechanics from The Pennsylvania State University in 2018. He is currently pursuing his PhD in Engineering Science and Mechanics, and his research interests include semiconductor reliability physics, emerging analytical technologies, and the application of electrically detected magnetic resonance to fundamental device physics research.

Stephen Moxim (Student Member, IEEE) graduated from The Pennsylvania State University with a bachelor's degree in Engineering Science and Mechanics, and is currently pursuing a PhD in Engineering Science and Mechanics. He has worked as a research assistant in the Semiconductor Spectroscopy Lab at Penn State since 2017. His research interests include the application of electrically detected magnetic resonance (EDMR) and near-zero-field magnetoresistance (NZFMR) to semiconductor device reliability problems. He has authored/co-authored 8 peer reviewed journal articles and submitted 2 more articles currently under review. He has contributed to 13 conference presentations.

Gaddi Haase received the Ph.D. degree in physical chemistry from the Hebrew University of Jerusalem, Israel, in 1989. After post-doctoral research at Columbia University, New York, NY, USA, and at the University of Wisconsin, Madison, WI, USA, he became a professor at the Chemical Physics Department, the Weizmann Institute of Science, Israel. In 2001, He then moved to Texas Instruments, where he engaged in process development and novel materials reliability research. He then moved to Molecular Imprints (nano-imprint lithography) and later joined the Microsystems Science and Technology Center at Sandia National Laboratories, Albuquerque, NM, USA, in 2011. He has over 35 peer reviewed papers and one patent.

David Hughart is a Principal Member of the Technical Staff at Sandia National Laboratories. He received his Ph.D. from Vanderbilt University in 2012. He has led projects investigating reliability characterization techniques for semiconductor devices and radiation effects experimentation and modeling, focusing on non-volatile memory. He has previously led wafer level reliability for Sandia's fab and helped develop Sandia's resistive memory technology.

Colin McKay earned his Ph.D. in Materials Science and Engineering from Penn State University. He now works at Sandia National Laboratories as an Electronics Engineer focused on semiconductor reliability physics and radiation effects.

Patrick Lenahan (Fellow, IEEE) is Distinguished Professor of Engineering Science and Mechanics and Co-Chair of the Inter-College Graduate Program in Materials Science and Engineering at Pennsylvania State University. After completing his Ph. D. at Illinois, he did a post-doc at Princeton University. Following the post-doc, in 1980, he joined Sandia National Laboratories, Albuquerque, NM, where he served as a member of the technical staff for five years. Since 1985 he has been with Pennsylvania State University. Patrick and his students have investigated reliability and materials physics problems in systems including the interfaces of silicon and silicon carbide with silicon dioxide, hafnium oxides, silicon nitrides, and a variety of low-dielectric constant materials. In recent years, his group has worked to develop various electrically detected magnetic resonance techniques to explore the structure and electronic properties of point defects in fully processed devices. The work has resulted approximately 230 journal articles, about 45 conference proceedings articles, about 400 conference presentations, and 4 patents. Patrick has been technical program chairman and general program chairman for the IEEE International Integrated Reliability Workshop and has also served on the technical program committee of the IEEE Semiconductor Interface Specialists Conference, the IEEE Nuclear Space Radiation Effects Conference, and the Rocky Mountain Conference on Magnetic Resonance; he has also served as either an invited or elected organizer of the MRS Electronic Materials Conference for many years.