Electron Spin Resonance Evidence that E'_1 Centers Can Behave as Switching Oxide Traps

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Abstract

We provide direct and unambiguous experimental spectroscopic evidence for the structure of a switching oxide trap in thermally grown SiO_2 gate oxides on Si. Switching oxide traps can "switch" charge state in response to changes in the voltage applied to the gate of a metal-oxide-semiconductor field-effect-transistor. Electron spin resonance measurements reveal that some E'_1 centers (a hole trapped at an oxygen vacancy) can behave as switching oxide traps.

I. INTRODUCTION

During the past decade, several groups characterizing the effects of switched bias "anneals" on trapped positive charge in metal-oxide-semiconductor field-effect-transistor (MOSFET) gate oxides have reported two distinct phenomena [1-11]. 1) A significant fraction of the total positive charge is attributed to "non-switching" or fixed oxide hole traps. 2) The remaining fraction of the total positive charge can repeatedly "switch" charge states with changes in gate bias. It is not clear whether or not this switching oxide charge can be permanently removed. Several different names have been proposed for these defects [1-11]. Some of the most widely cited designations include slow states, border traps, anomalous positive charge (APC), near interfacial oxide traps, and most recently, switching oxide traps. It is likely that all of these terms do not refer to the same defect. The key to differentiating between switching defects may lie in determining how the oxide was damaged. For example, the terms border traps [10] and switching oxide traps [4] refer to the post irradiation switching phenomena while the term APC was coined to refer to the switching phenomena observed after electron injection [5-7]. (Frietag, et al. [8,9] have also used the term APC to refer to post-radiation switching phenomena.) For reasons discussed in [4], we will use the term switching oxide trap to refer to the defects responsible for the post-irradiation switching phenomena.

It is known that charge trapping in amorphous insulating SiO_2 is dominated by microstructural defects. In order to understand the charge trapping behavior of thermal SiO_2, it is essential not only to characterize the electrical behavior of these defects, but to fully understand their structural nature. The structural nature of the defect primarily responsible for the hole traps near the Si/SiO_2 interface in high quality thermal oxide films gamma irradiated under positive gate bias was unambiguously identified as an oxygen vacancy related defect known as the E'_1 center [12]. (The structure of the E'_1 center is an unpaired electron localized on a Si backbonded to three oxygens [12,13].) The initial work has been confirmed by several later studies [14,15].

Oxide trapped charge has long been known to undergo a relatively slow long-term annealing. Oldham et al. [16], following the work of Manzini and Modelli [17], proposed that this process occurs as electrons tunnel into the oxide to neutralize the trapped holes (E' centers). Lelis et al. [2-4] later proposed that the switching behavior of oxide traps occurs because electron tunneling can occur in both directions — from the substrate to the E' center and back. Their model has not been universally accepted, however. Recently, Freitag et al. [8,9] proposed a two-defect model, in which the permanent annealing of some defects and the switching behavior of others are attributed to two different kinds of defects.

Following the work of Lenahan and Dressendorfer [12], Freitag et al. [8,9] take the defects that are permanently removed or annealed to be E'_1 centers. Following the nomenclature of Young et al. [5] and Trombetta et al. [6,7], they refer to the switching oxide traps as anomalous positive charge (APC). (As discussed later, we believe that this nomenclature may not be accurate since the defects are generated by radiation damage instead of electron injection.) In essence, they suggest that APC may be due to a hydrogen related defect [18] or some other defect — in any case, a defect as yet undetected by ESR.

The Single-Defect Model, proposed by Lelis et al. [2-4], suggests that a single defect, the E'_1 center, can account for both oxide hole traps and switching oxide traps. A key point to this model is that, due to variations in stress, there will be a distribution of separation distances between the two Si atoms in the E'_1 complex (O_Si+Si+O_Si). They suppose that an electron tunneling in from the silicon is trapped at the previously neutral Si of the previously positive E'_1 complex (O_Si+Si+O_Si), compensating the positive charge and pairing up with the unpaired electron. The neutral Si becomes negatively charged, restoring net neutrality, but in a dipole structure. At this point, one of two things can happen. 1) Sites in which the Si atoms at the ends of the dipole are "close" together will completely reform the Si-Si bond resulting in a configuration similar to that present before the initial hole capture. 2) Sites in which the initially positive and neutral Si are far enough apart will not completely reform.
The sites that reform to the initial configuration that was present prior to hole trapping are permanently annealed. Those sites that do not completely reform the broken bond remain as the switching oxide traps. In essence, if subsequent electron capture does not return the E' defect to its original precursor state, it could be a switching oxide trap.

Both the Two-Defect Model of Freitag et al. [8,9] and the Single-Defect Model of Lelis et al. [2-4] are supported primarily by electrical measurements which alone do not provide structural information. The authors of both these and other studies have called for ESR investigations of the phenomena [2-4,8,10].

In light of the existing (purely electronic) data, both of these models are plausible. However, since the Lelis model involves the widely studied E' defects, it is much more readily tested than the Freitag Two-Defect Model which would require searching for a defect which has never been observed.

In this paper, therefore, we test the validity of the Single-Defect Model by comparing ESR measurements of E' density before and after 24-hour switched bias sequences. We determine that E' centers can be switching oxide traps, confirming the basic premise of the Single-Defect Model.

II. EXPERIMENTAL DETAILS/RESULTS

Electron spin resonance measurements were performed at room temperature with a Bruker 200 series spectrometer with a calibrated "weak pitch" spin standard and a TE_{10} double resonant cavity. Spin densities, taken at non-saturating microwave power, have an absolute accuracy of better than a factor of two and a relative accuracy (for a series of measurements) of better than +/- 10%.

The oxides used in this study were prepared at Sandia National Laboratories using a radiation "hard" recipe. ("Hard" oxides were shown by Lelis et al. [2-4] to have a much larger density of switching oxide traps than soft oxides.) Oxides were grown at 1000°C in dry O_2 to a thickness of 120 nm on (111) p=200-400 Ω-cm p-type silicon. The samples received no post-oxidation anneal. The samples were then capped by a approximately 300 nm thick layer of lightly doped poly Si. The samples received no post-deposition anneal. The poly Si layer was removed with a 70 HNO_3:28 H_2O:3 HF etch before any measurements were taken in order to facilitate ESR analysis (poly-Si films contain large densities of trivalent Si centers that would complicate ESR detection of lower densities of E' centers).

In order to test the Lelis model, we first generated E' centers using a vacuum ultraviolet (VUV) hole injection scheme. The oxide surfaces were first positively biased with corona ions and then exposed to VUV photons (hc/λ = 10.2 eV) in an evacuated chamber. (The use of corona ions enabled us to avoid the use of a highly conductive gate material which would have seriously degraded the sensitivity of the ESR measurements.) The ions have essentially thermal kinetic energy and thus do not damage the surface of the oxide. The 10.2 eV photons are strongly absorbed within the top 10 nm of the oxide where they create electron-hole pairs [20]. Holes are driven across the oxide while electrons are swept out to remove positive corona charge. The number of injected holes, Q, is determined from \((C(ΔV))/e\) where C is the geometric capacitance of the oxide, ΔV is the difference between pre- and post- VUV Kelvin probe measurements, and e is the electronic charge.

Figure 1(a) shows the injection of approximately 5x10^{13} holes/cm² generates E' centers (g=2.0005). Figure 1(b) shows that no signals are detected prior to hole injection.

![Figure 1: ESR traces of thermally grown oxide film (a) before and (b) after hole injection.](image-url)

After the hole injection sequence, the samples were exposed to a series of alternating oxide bias anneals while E' density was monitored with ESR measurements. Oxide fields (applied with corona ions) of approximately +/- 3.5 MV/cm were held for at least 10² seconds. (These bias sequences approximately match those of earlier electronic studies [2-4,8,9]).

The effect of gate bias on E' density is shown in Figure 2. Point H+ shows E' density after hole injection. Point O1 shows that zero corona bias on the surface of the oxide does not substantially affect E' density; the change in E' density between point H+ and point O1 is less than our experimental error. Point NI shows that 24 hours at -3.5 MV/cm negative corona bias results in a significant increase in E' density. Point P1, taken after 24 hours of +3.5 MV/cm corona bias shows that E' density decreases with positive bias. This switching behavior of E' centers is repeatable, as seen in points N2 and P2. The fact that we can modulate E' density with changes in gate bias is unambiguous evidence that E' centers can act as switching oxide traps.

The Lelis model predicts that E' density will increase with negative bias and decrease with positive bias. Our ESR measurements from Figure 2 confirm this prediction. We find that, as predicted by the Lelis model, E' centers can account for both oxide hole traps and switching oxide traps. (This result is also consistent with an earlier spin dependent
recombination study [21] which indicated that some \( E'_c \) centers could respond to gate bias, and with a more recent ESR study that suggested but neither proved nor disproved that \( E'_c \) centers could behave as border traps [22].

![Graph showing \( E'_c \) density vs. various 24 hour bias sequences.](image)

**Figure 2:** \( E'_c \) density vs. various 24 hour bias sequences.

III. DISCUSSION

A. \( E'_c \) Centers Can Behave as Switching Traps

Our results are consistent with the basic premise of the Lelis single defect model: that after hole capture, subsequent electron capture does not return some \( E'_c \) defects to their original state. These are clearly switching traps. Our results, however, cannot distinguish between 1) electron capture at the neutral Si without subsequent reformation of the original Si-Si bond and 2) electron capture at either Si site accompanied by reformation of a significantly weakened Si-Si bond with greater separation and less stable bonding.

Our results do not preclude the possibility of other defects acting as switching traps in other oxides. For example, the switching behavior observed after electron injection known as anomalous positive charge (APC) may be due to another defect. This possibility is discussed in the next section.

B. Switching Oxide Traps, Near-Interface Oxide Traps, and Anomalous Positive Charge

When considering the complex nomenclature currently utilized to describe oxide charge trapping, two points are of primary importance: trap location and trap behavior. All hole traps in the oxide fall under the general heading of oxide traps. Oxide traps close enough to exchange charge with the silicon substrate may be considered near-interface oxide traps. "Close enough" can never provide an exact definition for these near-interfacial traps since the distance which charge may tunnel in (or out) of the oxide is dependent on the tunneling time (proportional to \( \log \text{t} \)). However, most experiments do not exceed \( 10^7 \) seconds and on this basis we may say that the near-interface oxide traps are within about 4 nm of the Si/SiO\(_2\) interface [23].

Near-interface oxide traps which are not permanently neutralized by electron tunneling and which repeatedly exchange charge with the silicon substrate are switching oxide traps. Our study clearly demonstrates that \( E'_c \) centers can behave as switching oxide traps. However, some near-interface traps undergo permanent annealing when they capture an electron, presumably by completely reforming the Si-Si bond broken during the initial hole capture. Thus, although switching oxide traps are near-interface oxide traps, not all near-interface oxide traps are switching oxide traps.

It is useful to consider the appropriateness of the term anomalous positive charge (APC) for radiation induced switching oxide traps. The reason this is an issue is because proponents of the Two Defect Model [9,10] have used the term APC to indicate traps which exchange charge with the substrate, differentiating them from the common oxide hole trap. The ESR evidence presented in this paper shows that it is not necessary to invoke a second defect (other than the \( E'_c \)) in order to explain switching oxide traps. In contrast, we shall show that the classic APC effect resulting from electron injection may be caused by an additional defect. There are several reasons to think that switching oxide traps are different from APC.

Figure 3 shows hole and electron injection data reported by Trombetta et al. [7] replotted on a log scale so that both curves are on the same scale. This Trombetta et al. experiment, performed with aluminum-gate capacitors, illustrates the classic APC effect. Whereas hole injection leads to a straightforward negative shift in the C-V characteristic, electron injection produces first a positive shift (as would be expected) followed at higher injection levels by an anomalous turnaround as if positive charge were suddenly being trapped. There are five points to make about this figure:

![Graph showing \( V_{th} \) vs. injected carriers. Generation of APC. Repotted from Trombetta et al. [7].](image)

1) For the purposes of this discussion, we define APC as the positive charge which causes the "turnaround" during avalanche electron injection [5-7] (this definition has roots in the literature). The electron fluence required to produce APC is
enormous compared to radiation experiments. The electron fluence generated by a 1 Mrad irradiation is indicated in Figure 3 — between three and four orders of magnitude below the levels at which APC is observed. (We note that the original concept of APC developed out of avalanche electron injection (AEI) experiments similar to this one. In avalanche injection experiments in general, the fields are low enough that only the injection polarity of carriers is present—either electrons or holes but not both. In AEI experiments therefore, APC is clearly due to injected electrons. In Fowler-Nordheim (FN) experiments, on the other hand, impact ionization normally occurs and both electrons and holes are present in the oxide. In general, separating the electron interactions from the hole interactions in the oxide is not a trivial exercise. Here and in the following discussions, we focus on the AEI results because they are easiest to interpret and because the concept of APC was originally developed from them. However, we acknowledge that our discussion does not explain all the FN results, which may be due to a qualitatively different defect.)

2) The data in Figure 3 was taken on Al-gate capacitors. Early studies on APC indicated that it was not observed in poly-gate samples. Our preliminary review of the literature indicates there is no published data showing APC (as we define it, APC reported by DiMaria et al. [25] was generated with Fowler-Nordheim Tunneling) in poly-gate samples. Radiation studies are normally done on poly-gate material.

3) APC is observed in AEI experiments only after a large buildup of negative charge has taken place [25]. This is a typical feature of APC — in fact, the "turn-around effect" is one of the other names for it commonly used in the literature. Feigl et al. [24] proposed that APC generation is a two-step process, where the first step is electron trapping, which conditions the defect so that something else can happen in the second stage. The second step, in the view of Feigl et al., is unclear but it evidently involves hydrogen. The Feigl et al. model seems to be still generally accepted as the explanation of the turn-around effect in AEI experiments. (Of course, it does not apply when no turn-around is observed.) The large buildup of trapped negative charge which is necessary for APC (and evident in Figure 3) is not observed in radiation studies.

4) APC as reported by Trombeta and others is neither neutralized nor removed by electron injection. In Figure 3, if one interrupted the electron injection at some point, one would not expect the charge to be removed by a subsequent electron injection. On the other hand, trapped holes are neutralized by electron injection. In fact, DiMaria [25] has argued that electron injection is a good way to tell trapped holes from APC — trapped holes will be neutralized, APC will be unaffected. In radiation studies of the Two-Defect Model [9,10], electrons were injected and the trapped positive charge was almost completely neutralized in a very short time. (The injection current was not monitored, so the number of electrons actually injected is not clear.) This result is qualitatively opposite to that reported for APC by Trombeta, which suggests that Frietag et al. were studying a different defect. Both injections were performed under positive bias, so switching caused by a bias polarity difference cannot explain the result.

5) APC generated by high electron fluence does not correlate with ESR results of E' centers in high field stressed oxides [26,27]. APC does correlate with the hydrogen content of the oxide and has been linked to hydrogen transport in the oxide.

All these points suggest that the switching behavior reported after irradiation damage is due to a different microstructural defect than the switching behavior known as APC. Our model of the switching E' is not intended to account for the right hand curve in Figure 3.

C. Processing

The presence or absence of switching oxide trapped charge depends on the specific process steps used to grow and anneal the oxide. Although there is wide variation in these process steps, a general pattern has emerged. We (Lelis and Oldham) have evaluated test chips from three high volume (soft oxide) commercial process lines (TI, National, and Micron) and three hardened process lines (TI, Sandia and Loral). We have not observed radiation-induced switching oxide traps in any of the three soft oxides; however, all three hard oxides exhibit significant switching behavior.

The Tl hard oxide and soft oxide differ in only one process step, the post-oxidation anneal (POA). The samples were prepared as a split lot where all the steps except oxidation and anneal were done on the same equipment at the same time. The oxidation temperature and ambient were the same (dry O2 at 1000°C). The soft Tl oxide received a POA typical of commercial oxides: when the oxide growth was complete, the flow of oxygen was cut off and the tube was purged by flowing Ar for 30 min at the oxidation temperature. On the other hand, the hard oxide was annealed by cutting off the heat and allowing it to cool with oxygen still flowing in the tube. This method of performing the POA has previously been shown to have a major impact on the radiation hardness of an oxide [28,29], as presented in the Figure 4.

Figure 4 shows V as annealing data for the hard and soft Tl oxides as a function of time following a 4 microsecond Linac pulse (both samples received the same dose). The oxides are slightly different thicknesses, so we plot \(\Delta V/\Delta n\) to normalize the data. At 100s, \(\Delta V/\Delta n\) in the soft oxide is more than an order of magnitude greater than for the hard oxide, as one might expect. However, at earlier times, the difference between the two oxides is much less because the hard oxide recovers much more quickly. It is possible that at very early times there may not be any difference at all between the two oxides. Because of photocurrent noise from the Linac pulse, the points between 10^3 and 10^4 sec have more experimental uncertainty than the later points. If we draw a smooth curve through the points after 10^3 sec as indicated in Figure 4, and we extrapolate back to the end of the Linac pulse at 4 microseconds, there appears to be no difference in the initial hole trapping of the two oxides. Even if one does not accept this extrapolation, there is a clear qualitative indication that the difference between the two oxides at early times (say 10^3 or 10^2 sec) is less than it is later because the hard oxide recovers more quickly. This
general trend was first pointed out by Oldham et al. [16] who suggested that the hole traps in hard oxides anneal faster because they are closer to the interface.

![Graph showing the annealing response of a hard and soft oxide.](image)

**Figure 4:** Room temperature annealing response of a hard and soft oxide.

There are two key points to be made here. First, Lelis and Oldham [4] showed that the soft oxide in Figure 4 has no measurable concentration of switching oxide traps and that the hard oxide has a high concentration of switching oxide traps. Remember these oxides differ only in their POA, that is, the one process step that was changed to harden a soft oxide also introduced switching oxide traps. Alternatively, one could say that changing the POA to harden the oxide caused fixed oxide traps to become switching oxide traps because the traps are closer to the interface.

The second point is that Deal [30] argued that what he called the negative-bias instability was due to incomplete oxidation—excess Si in the oxide near the interface. Deal showed that this instability could be eliminated by performing a high temperature (at the oxidation temperature) anneal in an inert ambient. From those results Deal inferred that the excess Si was being removed from the active region near the interface. (Deal’s excess silicon may an oxygen vacancy E’ precursor.) The high temperature POA has been a feature of commercial processes since Deal’s early work. The data in Figure 4 suggests that the oxygen deficiency is not really eliminated from the oxide, but rather diffused away from the interface into the bulk of the oxide. There it cannot readily charge exchange charge with the substrate, but can still contribute to radiation damage.

For the hard oxide, oxygen vacancies and the associated hole traps remain very near the interface where some exchange electrons reversibly with the substrate by the mechanism originally described by Lelis et al. This produces a harder but less stable oxide. In a very real sense, the hardness of the oxide depends on its instability.

The oxide used in this study was grown at 1000°C temperature in dry O₂ and did not receive a high temperature POA, similar to the hardened TI oxide in Figure 4. We are reasonably sure that the instability exhibited by radiation hardened oxides is related to the absence of the POA.

We note that typical industrial practice seems to be to do the POA at 900°C or 1000°C. This temperature seems to allow the redistribution of existing defects (oxygen vacancies) as well as creation of new defects. Since these temperatures are high enough to allow reflooding of glass, it seems reasonable that point defects can move about by diffusion. However if the temperature is increased enough, the oxide will tend to be substantially reduced creating very high concentrations of oxygen vacancies. This has clearly been shown for SIMOX-like anneals [31] at >1300°C. In addition, oxides annealed at 1100°C have high concentrations of oxygen vacancies near the interface [32,33]. These results are attributed to reduction of the oxide. In general, both processes may be present at all temperatures— redistribution of existing defects by diffusion and creation of new oxide defects by oxide reduction. At the temperatures where commercial fab lines do their POA, diffusion seems to be the dominant process. Oxide reduction clearly becomes more important at higher temperatures. Finally, since the three commercial processes we have evaluated represent a significant portion of the US semiconductor industry, we feel comfortable asserting that commercial oxides generally do not show radiation-induced switching oxide traps. However, commercial practice includes a great diversity of oxides, so we expect that if enough oxides are tested, at least a few exceptions will eventually be observed.

IV. CONCLUSIONS

Our results demonstrate that the basic premise of the Lelis Model, that E’ centers can behave not only as deep hole traps but also as switching oxide traps, is correct. However, the evidence we have presented cannot provide an extremely detailed verification of the model. In particular, we can not distinguish between 1) electron capture at the neutral silicon side of the E’ complex without subsequent reformation of the original Si-Si bond and 2) electron capture at the positive silicon side accompanied by reformation of a significantly weakened Si-Si bond with greater separation and less stable bonding. It is likely that the latter is correct.

Our results do not preclude the possibility of other defects acting as switching traps in other oxides. For example, in samples subjected to electron injection, it is very likely that the switching phenomena accompanying APC is caused by a different microstructural defect that the switching phenomena caused by radiation damage.

We have presented the first direct and unambiguous evidence for a structure involved in the switching oxide trap phenomena. Further work, however, will be necessary to fully determine the details of all oxide switching trap processes.

V. ACKNOWLEDGMENTS

Acknowledgment: We gratefully acknowledge support of the Defense Nuclear Agency and the Office of Naval Research,
contract #N00014-95-1-GO03. We also acknowledge Professor L.P. Trombetta for useful discussions. We acknowledge P.V. Dressendorfer of Sandia National Laboratories for providing samples.

VI. REFERENCES


