

Evidence for a Deep Electron Trap and Charge Compensation in Separation by Implanted Oxygen Oxides

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Abstract

We present direct evidence for the creation of deep electron traps in Separation by IMplantation of OXYgen buried oxides. In addition, we present combined electrical and electron spin resonance evidence which demonstrate that at least some positively charged paramagnetic E' centers are compensated by negatively charged centers. Finally, we present evidence which strongly suggests that a substantial fraction the deep electron traps are coupled to E' centers.

I. INTRODUCTION

Silicon-on-insulator (SOI) technologies may have several advantages over conventional silicon technologies. These advantages include high speed, elimination of latch-up, and transient radiation hardness [1].

By definition, SOI device structures have a buried oxide layer. A process known as Separation by the IMplantation of OXYgen (SIMOX) is arguably the technology of choice for the formation of that layer. In SIMOX, the buried oxide layer is created by ion implanting a high dose of oxygen ions ($>10^{18}$ / cm^2) at a high energy (~ 200 keV) into a silicon wafer. A subsequent high temperature ($\sim 1300^\circ\text{C}$) anneal step allows for formation of high quality Si/SiO₂ interfaces [2].

In several potential applications, the radiation or hot carrier response of the buried oxide is an important reliability issue. Both radiation and hot carrier damage can involve the capture of charge carriers in the buried oxide. These trapped charge carriers can cause threshold voltage shifts and back channel leakage in SOI structures. Before SOI structures can be fully exploited, it is essential to understand the mechanisms of charge trapping in the buried oxide layer.

In our effort to understand the charge trapping properties of the buried oxide, we have studied the response of SIMOX oxides to ionizing radiation with a combination of electron spin resonance (ESR), capacitance vs. voltage (CV) electrical measurements, and charge injection sequences. ESR has been useful in the past in identifying the structure of point defects in amorphous thin films [3-8]. When combined with CV measurements and a variety of charge injection sequences, ESR enables structural identification of the point defects responsible for charge trapping [6-8].

In this paper, we present strong evidence for the creation of a deep electron trap in SIMOX [9]. We also present evidence that electron traps compensate for trapped positive charge. Our work indicates that at least some of the electron traps are created or stabilized by, in effect coupled to, positive charge. Much of the positive charge resides in E' centers. The E' center is an unpaired electron residing on a silicon bonded to

three oxygens [10, 11]. In the thermally grown gate oxides of conventional metal/oxide/silicon (MOS) devices, the E' centers is a hole trapped in an oxygen vacancy [9].

II. BACKGROUND

During the past two and one half years, we have studied point defects in SIMOX oxides with a combination of ESR and CV measurements. [9, 12-16] We previously reported that very high densities ($\sim 10^{18}/\text{cm}^3$) of E' centers are generated in SIMOX buried oxides which have been exposed to vacuum ultraviolet (VUV) irradiation ($hc/\lambda \leq 10.2\text{eV}$). This work clearly showed that a very high density of E' precursors is distributed throughout the buried oxides. We also searched for other ESR spectra in the range of the free electron g value but were unable to detect other signals. Although we looked specifically for the "amorphous silicon" defect spectra reported present in high densities ($\sim 10^{14}$ / cm^2) by Stessmans, Revesz, and Devine [17], we were unable to observe it with a detection limit of $\sim 10^{11}$ spins / cm^2 . (We now observe qualitatively and quantitatively similar results in ⁶⁰Co gamma irradiated SIMOX oxides. We therefore feel that our VUV results are relevant to gamma and X-ray radiation damage.)

In our earlier observations, we noted that the creation of high densities of E' centers was accompanied by virtually no net space charge (< 1 volt shift from origin) in the buried oxide [13-16]. This absence of net space charge ($< 4 \times 10^{11}$ / cm^2) combined with the large density of E' centers ($\sim 4 \times 10^{13}/\text{cm}^2$) suggested two possibilities [13-16]: 1) that SIMOX E' centers are neutral, or 2) that at least some SIMOX E' centers are positively charged (E' centers are the dominant deep hole trap in thermal oxides [8].) and compensated by an equal number of negatively charged centers.

In order to test these possibilities, we performed a series of charge injection experiments [12-16]. We found that by injecting electrons into VUV illuminated oxides we reduced E' amplitude. We also found that by injecting holes into the oxides we increased E' amplitude [14-16]. These results demonstrated that at least some of the E' centers in SIMOX buried oxides are positively charged. However since after VUV illumination the density of E' centers is much greater than the total charge density [13-15], the results also suggest that some of the positively charged E' centers are compensated by trapped electrons. Zvanut, et al. [18] recently concluded that E' centers in hydrogen treated SIMOX are electrically neutral.

III. EXPERIMENTAL DETAILS

A. Samples

The samples used in this study include p<100> 405 nm single implant SIMOX oxide and n<100> 385 nm multiple implant SIMOX oxide samples. Both single and multiple implant samples received a five hour anneal in 99.5% argon and 0.5% oxygen at 1325 °C. (An anneal above 1300 °C allows the formation of device quality interfaces and makes SIMOX technologically relevant [2].) A residual oxide and the superficial silicon layer were removed by subsequent etches in HF and then KOH at room temperature. (Although the KOH etch did not significantly affect the results presented in this paper, we find that extended KOH exposure can result in the creation of hydrogen related point defects in the buried oxides. Space limitations do not permit a full discussion of these KOH results here [19]. (Buried oxides without the superficial silicon layer will be designated as "bare".) The behaviors of the E' centers in multiple and single implant oxides were qualitatively the same although some quantitative differences were observed in spin densities.

B. Electron Spin Resonance

Our ESR measurements were conducted at room temperature on a state of the art commercial X-band spectrometer with a TE₁₀₄ "double" resonant cavity and a calibrated "weak-pitch" spin standard. This system permits measurements of relative spin densities accurate to within 10% and absolute spin densities accurate to within a factor of two.

C. Capacitance vs. Voltage

Net oxide space charge density was determined from mid-gap shifts in high frequency CV curves. CV measurements were taken at room temperature using a 1 MHz capacitance bridge and a mercury probe. (Etchback experiments indicated charge trapping throughout the oxides [12-14].)

D. Generation of E' Centers

In most of our experiments, E' centers were generated by exposing bare buried oxides to VUV light from a 50 watt deuterium lamp. Bare buried oxides were VUV illuminated ($hc/\lambda \leq 10.2$ eV) without bias for an extended period (40 hours). Exposing the samples to this extended VUV illumination generates extremely high densities of E' centers throughout the oxide ($\sim 10^{18}$ / cm³) with no net oxide charge. The approximate dose for our VUV irradiations was determined by estimating the number of electron/hole pairs generated during VUV illumination under bias as compared to the number of pairs created by gamma irradiation under comparable bias. The approximate dose for VUV irradiation is about 100 Mrads(SiO₂).

In some experiments, buried oxides were exposed to approximately 210 Mrad(SiO₂) of ⁶⁰Co gamma irradiation. The superficial silicon overlayer of these oxides was not removed prior to irradiation, nor was a bias applied to the surface of the oxide.

In addition, as discussed below, some buried oxides were exposed to VUV illumination from a notch filtered ($hc/\lambda = 10.2$ eV) VUV lamp while the oxides were under positive bias.

E. Charge Injection

1. Biasing during charge injection

Most of our experiments involve injecting electrons and holes into large area (~ 1 cm²) buried oxide/silicon samples suitable for ESR measurements. We applied a uniform electrical bias across our samples using corona discharge ions. Positive bias was applied across the buried oxides by depositing corona discharge ions on the exposed buried oxide surface. (These ions have essentially thermal kinetic energy and do not damage the oxides [21].) Corona charging allowed for the generation of a uniform bias, in effect a transparent gate, over the large surface area samples (~ 1 cm²) required for ESR measurements. This corona bias allowed for the injection of electrons and holes into the oxides. Surface potentials were measured with a Kelvin probe electrostatic voltmeter. The oxides were generally charged to a potential of about 100 volts.

2. Electron injection

Electrons were injected into the oxides using ultraviolet illumination (UV) from a sub-SiO₂ bandgap ($hc A \leq 5.5$ eV) mercury-xenon lamp in combination with a positive corona ion bias. The brief (seconds) UV illumination results in the internal photoemission of electrons from the Si into the SiO₂. The positive bias drives electrons across the buried oxide. When the electrons reach the surface of the oxide, they recombine with the positive charge of the corona ions. Using a Kelvin probe, we evaluate the loss in surface potential due to the electron/corona ion charge recombination, ΔV . We calculate the injected electron density from $(C_{\text{oxide}})(\Delta V) = Q$. (In a typical injection sequence, the surface potential of the oxides begins at about 100 volts and is reduced to about 10 to 20 volts.)

3. Hole injection

Holes were injected into the buried oxides using VUV light from a 50 Watt deuterium lamp with a 10.2 eV notch filter. The filter passes only photons with $hc/\lambda = 10.2$ eV which are absorbed in the top 10 nm of the oxide, where they create electron hole pairs [21,22]. The oxides were illuminated briefly (minutes) while positively biased. The positive bias drives holes across the oxide while electrons are swept out to the oxide surface where they recombine with the positive charge of the corona ions. We use a Kelvin probe to evaluate the loss in surface potential, ΔV , and (as we do for electron injection) calculate the injected hole density from $(C_{\text{oxide}})(\Delta V) = Q$. (In a typical hole injection sequence, the surface potential would be approximately 100 volts prior to VUV exposure and reduced to 10 to 20 volts by the exposure.)

F. Charge Cycling

In our charge cycling experiments, we inject charge of one sign into the buried oxide (about $5 \times 10^{13} / \text{cm}^2$) and then make ESR and CV measurements to measure E' spin density and net oxide charge. After these measurements, we inject approximately equal numbers (about $5 \times 10^{13} / \text{cm}^2$) of charge of opposite sign. We repeat this process several times.

IV. EXPERIMENTAL RESULTS AND ANALYSIS

Figure 1 shows a comparison of ESR spectra of samples which were a) ^{60}Co gamma irradiated to about 200 Mrads(SiO_2) or b) VUV illuminated to about 100 Mrads(SiO_2). In both sets of SIMOX samples (taken from same wafer) a large density of paramagnetic E' centers (about $10^{18} / \text{cm}^3$) is created.

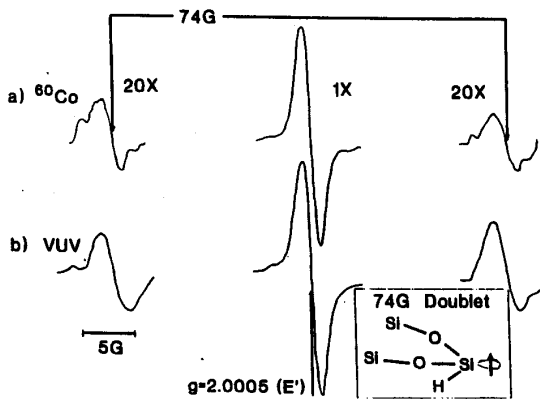


Figure 1: Comparison of effects of (a) Co^{60} and (b) VUV irradiation on SIMOX buried oxides. Large central resonance at $g = 2.0005$ is due to simple E' centers. The smaller "bumps" on either side are due to hyperfine interaction of hydrogen complexed E' centers called 74G doublets.

CV measurements of both VUV and ^{60}Co irradiated samples indicate mid-gap shifts of less than 2 volts for VUV irradiated and about -20 volts for ^{60}Co irradiated; both indicate far less positive charge than E' density. The two side lines on either side of the main E' resonance are due to hydrogen complexed E' centers known as 74G doublets [23,24]. (Hydrogen has a magnetic moment of $1/2$ and thus splits the central E' resonance into two lines separated by 74G.) The 74G doublet signal is due to an E' center in which the silicon with the unpaired spin is bonded to two oxygens and a hydrogen [23,24]. In both the VUV and ^{60}Co irradiated samples, these hydrogen related E' centers comprise about 3-5% of the total E' resonance. This value is of some interest; Vitko [24] reported about 5% abundant 74G doublet centers in heavily irradiated "wet" bulk SiO_2 and undetectable levels in

"dry" bulk SiO_2 . Our results, to the best of our knowledge, represent the first direct experimental observation of a specific hydrogen related point defect in SIMOX buried oxides. A more extensive discussion of these and other hydrogen experiments is given in another paper appearing in this issue. [25]

Figure 2 shows the quantitative response of VUV irradiated single implant SIMOX oxides to hole/electron charge injection. (Charge injection is described in the Experimental Details section.) These oxides were first exposed to about 40 hours of unfiltered VUV illumination ($hc/\lambda \leq 10.2\text{eV}$) prior to charge cycling. Consistent with earlier work [11-16], the 40 hours of VUV illumination results in a large E' density (figure 2b) with little or no net space charge (figure 2a). The initial hole injection point (H1 in figure 2a) shows that about 1.6×10^{13} holes / cm^2 are captured. Since about 5×10^{13} charges / cm^2 were injected in the initial hole injection sequence, this space charge buildup indicates a large capture cross section for buried oxide hole traps. Point H1 in figure 2b shows that about 0.8×10^{13} E' centers are created in the initial hole injection sequence. The trapped hole and E' densities match within a factor of two (within experimental error). Next, we injected electrons into the oxide. The electron injection, E1, results in the subsequent capture of about 1.7×10^{13} electrons / cm^2 (see figure 2a, point E1) and the loss of about 1.0×10^{13} E' / cm^2 . These numbers also match within experimental error and also indicate a large capture cross section for sites involved in electron trapping.

For the entire charge injection cycling sequence, the CV results in figure 2a show that the amount of trapped charge cycles with almost perfect repeatability: about 1.5×10^{13} charges are captured on each subsequent charge injection. (Note that the positive shifts indicate electron trapping.) The ESR E' density data from figure 2b shows that the E' magnitude also cycles back and forth repeatably, changing about 0.8×10^{13} spins per cycle. This matches our CV data within a factor of two and shows that paramagnetic E' centers site are capturing electrons to become diamagnetic and diamagnetic E' precursors or diamagnetic E' center sites are capturing holes, both with a large capture cross section ($\sim 10^{-13} \text{cm}^2$).

Figure 3 shows results of the experiment of figure 2 with one change: this time we inject electrons first instead of holes. Once again, the oxides were illuminated with unfiltered VUV light for about 40 hours prior to charge injection. The initial post VUV electron injection (point E1) results in the net buildup of about 0.2×10^{13} electron / cm^2 and the loss of about 0.9×10^{13} E' / cm^2 . The difference between these numbers falls outside of our experimental error. The fact that the decrease in paramagnetic E' centers is much greater than the net number electrons captured is very peculiar.

A possible explanation involves a coupling between E' centers and electron traps. The explanation is as follows: in order to render a paramagnetic (ESR visible) defect diamagnetic (ESR invisible), the defect has to either capture or lose an electron. (We take the defect to be paramagnetic when it has an odd number of electrons; the loss or gain of an electron yields an even number of electrons and a diamagnetic site.) Since an excess of electrons is present during electron

injection, it is very unlikely that the E' defects are losing electrons. It is much more likely that the paramagnetic E' center sites are capturing electrons. Therefore, since about 0.9×10^{13} E' / cm² are rendered ESR invisible, we assume that about 0.9×10^{13} electrons / cm² are captured by these E' centers. Furthermore, let us assume that for every one of these electrons captured by (presumably positively charged) E' centers, a nearby trapped electron is detrapped because the positive charge it was coupled to has disappeared. This explanation would be consistent with the lack of net positive charge in the oxide prior to electron injection. It is also consistent with the annihilation of a large amount of E' centers with electron injection without a simultaneous buildup of net negative charge in the oxides.

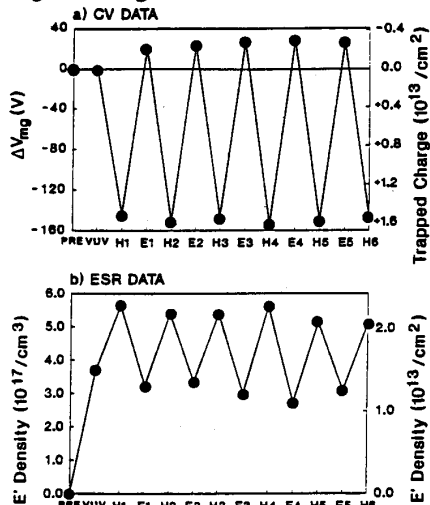


Figure 2: Effects of charge injection on (a) CV and (b) ESR measurements of VUV illuminated buried oxides.

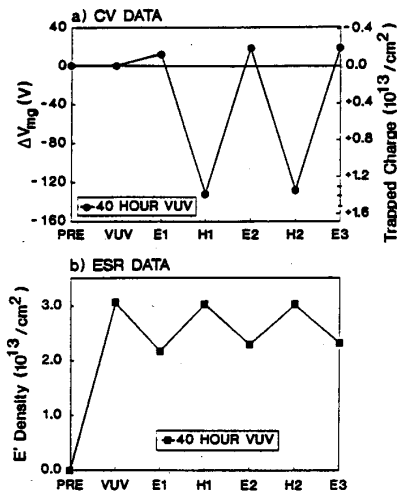


Figure 3: Effects of charge injection on (a) CV and (b) ESR measurements of VUV illuminated buried oxides.

The subsequent hole injection (H1) results in the net capture of 1.5×10^{13} holes / cm² and an increase in E' density of about 0.9×10^{13} E' / cm². Unlike the initial electron injection results, these densities match within a factor of two.

After the initial electron injection, the amount of trapped charge cycles with almost perfect repeatability with about 1.5×10^{13} charges captured on each subsequent charge injection. Beginning with the initial electron injection, the E' density cycles back and forth, changing about 0.8×10^{13} spins / cm² per cycle.

The fact that CV measurement of space charge and ESR measurements of spin density do not "match" after the initial electron injection but do match fairly well after subsequent hole injection suggests that some change may have occurred at the trapping sites as a result of the initial irradiation. To determine whether or not this is the case, we examine unirradiated oxides.

Figure 4 shows the effects of electron and hole injection into unirradiated multiple implant SIMOX buried oxides. No paramagnetic signals could be observed in the oxides prior to charge injection. Figure 4a shows that photoinjection of 5×10^{13} electrons / cm² into an unirradiated buried oxides does not generate a measurable paramagnetic signal. CV measurements indicate virtually no net space charge; very few electrons are trapped.

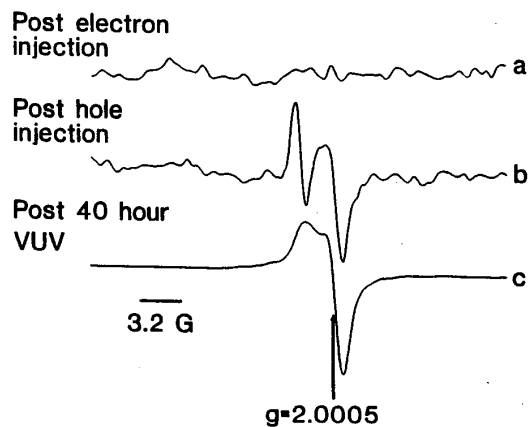


Figure 4: ESR traces of SIMOX oxide (a) after the injection of about 10^{14} electrons/cm² and (b) after the injection of about 10^{14} holes/cm². (Note the strong signal at $g=2.0005$ after hole injection.)

Figure 4b shows that injection of 5×10^{13} holes / cm² into unirradiated buried oxides results in a fairly strong paramagnetic E' signal (5×10^{16} spins / cm³) accompanied by a large (-170 V) negative CV shift. The fact that electron injection does not generate E' centers while hole

injection does generate E' centers strongly indicates that at least some of the E' centers are related to positive charge. (Note however, that there is not a one to one correspondence between E' centers and positive charge here [13-16]. Therefore E' centers may not account for all of the positive charge.) The peculiar lineshape (compare to figure 4c) of the hole injection induced E' suggests that changes in the local environment of the E' unpaired spin may occur with long VUV exposure. Note also the absence of electron trapping in the unirradiated oxide. In VUV irradiated oxides (figures 2 and 3), injection of the same number of electrons resulted in a substantial buildup of negative space charge.

In figure 5, we directly compare the electronic response of both VUV illuminated and unilluminated multiple implant SIMOX oxides to electron injection. After the injection of about 3×10^{13} electrons/cm², quite substantial ($>10^{12}$ /cm²) net negative charge buildup occurred in the VUV irradiated sample but little or no net negative charge appeared in the unirradiated sample. (Etchback studies show the net negative charge to be distributed in an approximately uniform manner throughout the oxide.) This is unambiguous evidence that VUV illumination generates deep electron traps. A possible explanation as O'Reilly and Robertson [26] have proposed, is that the positively charged E' centers create electron trapping levels. At any rate, the results clearly show that irradiation some way creates electron trapping in the oxide.

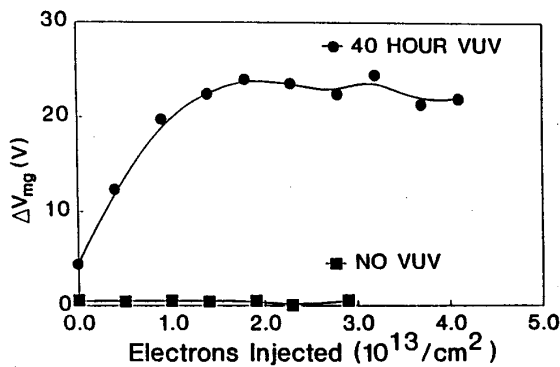


Figure 5: Shown here are CV shifts of a VUV irradiated oxide and an unirradiated oxide subjected to similar electron injection. Substantial electron trapping occurs in the VUV irradiated samples while little or no trapping occurs in the unirradiated sample.

Figure 6 completes our comparison of unirradiated and VUV irradiated oxides. It illustrates the effects of charge cycling on unirradiated single implant SIMOX oxides. Beginning with the initial hole injection, charge is cycled repeatedly (1.3×10^{13} /cm² charges/cycle). But, as figure 6b shows, the ESR results do not closely match the electrical

measurements. While the number of trapped charge carriers cycle repeatably, the number of paramagnetic E' centers grows by a substantial amount after each hole injection sequence. This is the result of a "baseline shift" from our hole injection technique. The hole injection technique eventually involves many minutes of VUV exposure which, even without any bias applied, continually creates some new E' centers that accumulate and add to the baseline. Even after accounting for this "baseline shift", the changes in E' density and trapped charge density are still not equal within experimental error. Although at least some E' centers are positively charged, a simple one to one correspondence between E' centers and net positive charge does not exist in SIMOX oxides. SIMOX charge trapping is much more complicated than trapping in thermal SiO_2 in which a simple one to one correspondence between E' and positive charge is at least approximately satisfied [8].

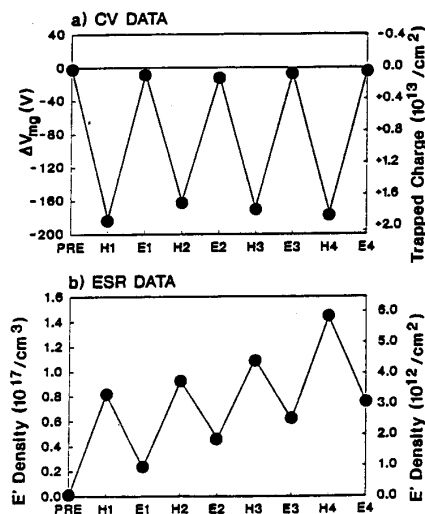


Figure 6: Effects of charge injection on (a) CV and (b) ESR measurements of unilluminated buried oxides.

V. DISCUSSION

We demonstrate the importance of E' centers in SIMOX charge trapping through the results of the three charge cycling experiments (shown in figures 2, 3, and 6). These three experiments show that paramagnetic E' center sites capture electrons and that both diamagnetic E' precursors and diamagnetic E' center sites capture holes with large capture cross sections. In the VUV illuminated samples of figure 2, the charge injection induced changes in charge density and E' density were within a factor of two of one another. This result establishes a clear link between E' centers and positive charge in SIMOX. This observation is corroborated by the data in figure 4. In figure 4 we see that, in unirradiated oxides, hole injection results in generation of E' centers and trapped positive charge while electron injection does not. At least some SIMOX paramagnetic E' centers are positively charged.

The behavior of the SIMOX E' centers is complex. When VUV irradiated oxides and unirradiated oxides are subjected to similar levels of electron injection, the VUV irradiated oxides build up a substantial amount of net negative charge; the unirradiated oxides do not. However, despite this negative charge buildup, the decrease in VUV illuminated oxide E' density still considerably exceeds the net change in oxide space charge. Initially, VUV generated E' centers are not accompanied by much net oxide space charge. Since these paramagnetic E' center sites do capture electrons with large capture cross section, we provisionally assume that they must (at least in some cases) be positively charged and compensated by negatively charged electron traps. These electron traps do not appear to be present prior to VUV irradiation (figure 5). According to O'Reilly and Robertson [26], electron trapping levels in amorphous SiO₂ could be created by positive charge in a nearby trapping center E' site. Our results seem to be consistent with the O'Reilly and Robertson work.

The presence of shallow electron traps in SIMOX oxides were discovered by Boesch et al. [27] but in his study, the trapped electrons were detrapped well below room temperature. The electron traps indicated by our study are significantly different from those of the Boesch et al. study; our electron traps are stable at room temperature.

Our results regarding the compensation of positively charged E' sites with trapped electrons may be of some relevance to the thermally grown oxides of conventional MOS technology. Quite recently, Fleetwood et al. [28] have argued that a significant fraction of E' trapped positive charge in thermal oxides is compensated by trapped electrons. Although the charge compensation proposed by Fleetwood, et al. does not appear to be so nearly complete as we find in SIMOX, the levels of compensation they estimate are substantial (16% to 40%).

VI. CONCLUSION

We have presented, to our knowledge, the first direct evidence for the creation of deep electron traps in SIMOX buried oxides. Our results strongly suggest a coupling of electron trapping levels with E' sites. Our results indicate that a substantial fraction of the E' sites in SIMOX buried oxides are positive and compensated by trapped negative charge.

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