Electron spin resonance evidence for the structure of a switching oxide trap: Long term structural change at silicon dangling bond sites in SiO_2

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(Received 30 May 1995; accepted for publication 4 August 1995)

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'_γ centers (a hole trapped at an oxygen vacancy) can behave as switching oxide traps.

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 ''nonswitching'' 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, 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 postirradiation 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 postradiation switching phenomena.) For reasons discussed in Ref. 4, we will use the term switching oxide trap to refer to the defects responsible for the postirradiation switching phenomena.

It is known that charge trapping in amorphous insulating SiO_2 is dominated by microstructural defects. In order to fully 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 oxide hole traps near the Si/SiO_2 interface was unambiguously identified in high quality thermal oxide films as an oxygen vacancy related defect known as the E'_γ center.[12] (The structure of E'_γ center is an unpaired electron localized on a Si backbonded to three oxygens.[12,13]) The original 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 completely 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'_γ 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 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'_γ 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 in the amorphous SiO_2, there will be a distribution of separation distances between the two Si atoms in the E'_γ complex ($O_3 \equiv Si\cdot + Si \equiv O_3$). Now, suppose an electron tunneling in from the silicon is trapped at the previously neutral Si of the previously positive E'_γ complex, compensating the positive charge and pairing up with the unpaired electron ($O_3 \equiv Si$: $+ Si \equiv O_3$). 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

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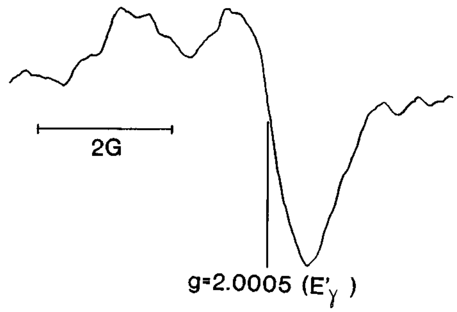

FIG. 1. Post-hole injection ESR trace of thermally grown oxide film.

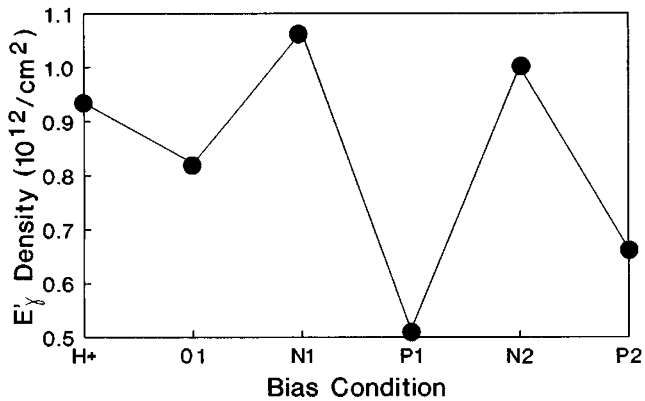

FIG. 2. E' density vs various 24 h bias sequences.

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 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'_γ 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 data, both of these models are plausible. However, due to the nature of the Lelis model (it involves the widely studied E'_γ defect), it is much more readily tested than the Freitag two-defect model which would require searching for a defect which has never been observed.

Therefore, in this letter, we test the validity of the single-defect model and, in the process, determine that E'_γ centers can be switching oxide traps. We do this by comparing ESR measurements of E'_γ density before and after 24 h switched bias sequences. (These bias sequences approximately match those of both electronic studies.[2–4,8,9])

ESR measurements were performed at room temperature with a Bruker 200 series spectrometer with a calibrated "weak pitch" spin standard and a TE_{104} "double resonant" cavity. Spin densities, taken at nonsaturating 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 $\pm 10\%$.

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 to a thickness of 120 nm in dry O_2 on (111) $\rho = 200-400\ \Omega$ cm p-type silicon. The samples were then capped by an $\sim$300 nm thick layer of lightly doped poly-Si. The poly-Si layer was removed with a 70 NHO_3:28H_2O:3 HF etch before any measurements were taken.

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[18,19] and then exposed to VUV photons ($hc/\lambda = 10.2$ eV) in an evacuated chamber. 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 $[C(\Delta V)]/e = Q$ 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 shows that the hole injection sequence generates E'_γ centers (g=2.0005). We will show that a significant fraction of E'_γ defects can behave as switching oxide traps.

After the hole injection sequence, the samples were exposed to a series of alternating oxide bias anneals while E'_γ density was monitored with ESR measurements. Oxide fields (applied with corona ions) of approximately ± 3.5 MV/cm were held for at least 10^5 s. (Several studies have indicated that the switching oxide trap response saturates after $\sim 10^5$ s under negative bias.)

The effect of gate bias on E'_γ density is shown in Fig. 2. Point H^+ shows E'_γ density after hole injection. Point *01* shows that neutral oxide bias does not substantially affect E'_γ density. (The charge is less than our exerimental error.) Point *N1* shows that 24 h at -3.5 MV/cm negative bias results in a significant increase in E'_γ density. Point *P1*, taken after 24 h of $+3.5$ MV/cm bias shows that E'_γ density decreases with positive bias. This switching behavior of E'_γ is repeatable, as seen in points *N2* and *P2*. The fact that we can modulate E'_γ density with changes in gate bias is unambiguous evidence that E'_γ centers can act as switching oxide traps.

The Lelis model predicts that E'_γ density will increase with negative bias and decrease with positive bias. Our ESR measurements from Fig. 2 confirm this prediction. We find that, as predicted by the Lelis model, E'_γ centers can account for both oxide hole traps and switching oxide traps. (This result is consistent with an earlier spin dependent recombination study of Jupina *et al.*[21] which suggested that some E' centers could respond to gate bias). Our results do not preclude the possibility of other defects acting as switching traps in other oxides. For example, it is very likely that the switching phenomena accompanying APC in electron injection damaged oxides is due to a completely different microstructural defect than the switching phenomena in irradiation damaged oxides.

Our results are consistent with the basic premise of the Lelis single defect model: that after hole capture, subsequent electron capture may not return the E'_γ defect to its 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 the positive Si site accompanied by reformation of a significantly weakened Si–Si bond with greater separation and less stable bonding.

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

We gratefully acknowledge support of the Defense Nuclear Agency and the Office of Naval Research, Contract No. N00014-95-1-G003. We thank Professor L. P. Trombetta for useful discussions.

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