Observation and electronic characterization of two E' center charge traps in conventionally processed thermal SiO₂ on Si

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(Received 4 February 1994; accepted for publication 25 August 1994)

We demonstrate that at least two varieties of E' defect precursors exist in a wide variety of conventionally processed thermal SiO₂ thin films. We provisionally label the defects EP and $E'_{\gamma p}$. We find that EP defect capture cross sections exceed the corresponding $E'_{\gamma p}$ values by an order of magnitude, that EP centers are distributed far more broadly throughout the oxides than are the $E'_{\gamma p}$ defects, and that the EP resonance, unlike the $E'_{\gamma p}$ resonance is not stable at room temperature. © 1994 American Institute of Physics.

Charge trapping in gate oxides is an important reliability concern since charge traps determine the electronic properties of amorphous insulators. In the early 1980s, the work of Lenahan and Dressendorfer¹⁻³ showed that E' centers dominate charge trapping in irradiated thermal SiO₂ thin films. (E' centers are paramagnetic oxygen deficient silicon sites in)the oxide.³) This work was confirmed by a number of later studies.⁴⁻⁸ For quite some time, no explicit distinction was made with regard to possible variations in E' line shapes or structures in thin SiO₂ films. Recently though, a menagerie of "new" E' variants^{9–19} has been reported, almost entirely in exotic SiO_2 thin films. The new E' variant observations include a "peculiar" line shape in separation by implanted oxygen (SIMOX) buried oxides,^{9,10} the 10.4 G doublet^{11,12} and 74 G doublet^{11,13,14} hydrogen complexed E' center spectra, the "EX" center¹⁵ in home grown thermal SiO₂, the "*EH*" center¹⁶ in bond and etchback (BESOI) buried oxides, and E'_{δ} -like centers.^{5,17–19} The "*EX*", "*EH*", E'_{δ} , and "peculiar line shape" observations all involve a sharp line shape with a zero crossing $g \cong 2.002$, similar to a line shape observed in bulk fused silica by Griscom and Friebele.²⁰

In this letter, we compare electronic properties of two E' variants which can be generated in a variety of thermally grown thin oxide films. The appropriate names for thin film E' variants is now in a confusing state of flux. Some years ago, Griscom *et al.*^{20,21} proposed a nomenclature (i.e., E'_{α} , E'_{β} , E'_{γ} , E'_{δ}) for several E' variant spectra which they had observed in bulk fused silica. Although the Griscom *et al.*^{20,21} nomenclature is reasonable on the basis of their bulk SiO₂ studies, a simple transfer to thin-film spectra (which they never intended) is probably impossible. However, two of the Griscom and Friebele line shapes appear to be relevant to our study: the E'_{γ} and E'_{δ} . Unfortunately, their proposed models for these defects are either wrong in some aspects or nonunique and thus not applicable to the thin-film data.^{17,22–24}

Therefore, in order to minimize confusion, we refer to the two E' variants of our study as $E'_{\gamma p}$ for positively charged E'_{γ} centers and EP for our E'_{δ} -like line shape. The EP indicates a Provisional \underline{E}' assignment. (Aside from the Griscom and Friebele bulk SiO₂ study,²⁰ we are unaware of any other convincing evidence regarding the detailed structure associated with E'_{δ} -like line shapes.) With a combination of electron spin resonance (ESR) and charge injection schemes, we find that paramagnetic *EP* centers are positively charged hole traps with extremely large capture cross sections for holes when neutral and electrons when positively charged, in both cases significantly larger than that of $E'_{\gamma p}$ centers. We also find that EP centers, unlike $E'_{\gamma p}$ centers, are distributed broadly throughout the oxide and are not stable at room temperature.

Several sets of oxides were used in this study. One set denoted Harris (Cl), were exposed to significant amounts of Cl during processing. The Cl was introduced during oxide growth by addition of trichloroacetylene (TCA) to the oxidizing ambient. These pyrogenic steam oxides were grown to a thickness of 35 nm at 800 °C on lightly doped ($\rho \sim 100$ Ω cm) (111) *n*-type Si substrates at the Harris Semiconductor facility at Findlay, OH, in an ambient with an O₂ flow rate of 3250 sccm, a H₂ flow rate of 3500 sccm, and a TCA flow rate of 50 sccm. After oxidation, they were annealed for 10 min in N2 at 1050 °C. Another set of oxides, denoted Harris (REOX), is identical to the Harris (Cl) except that it was exposed to an additional 800 °C reoxidation step. Other oxides, denoted Harris (no-Cl), were not exposed to Cl. The no-Cl oxides were grown by Harris Semiconductor facility in Melbourne, FL to 850 nm on $\rho \sim 3-5 \Omega$ cm (100) *n*-type Si substrates. A 120 nm oxide was grown in steam on 40 Ω cm (111) Si by Sandia National Laboratories. After oxidation, a polysilicon gate was deposited. After gate deposition, the structure was subjected to an 1100 °C anneal in N_2 . (The polygate was removed before any measurements were taken.) Oxides grown in steam on high resistivity (111) Si at 900 °C for 95 min to 38 nm were prepared at a university facility.

ESR measurements were performed at room temperature on a Bruker Instruments X-band spectrometer. Relative spin densities are accurate to $\pm 10\%$ while absolute numbers are accurate to within a factor of two.

In order to generate and annihilate the *EP* and $E'_{\gamma p}$ center signals, the oxides were flooded with holes and electrons. We flooded oxides with holes by positively biasing the oxide surfaces with corona ions^{25,26} and then exposing the oxide surfaces to vacuum ultraviolet (VUV) photons ($hc/\lambda = 10.2$ eV) in an evacuated chamber. The 10.2 eV photons are absorbed primarily in the top 10 nm of the oxide where they



FIG. 1. ESR traces of several different thermal oxide films after hole injection. Spectrometer settings were chosen to maximize visibility of the *EP* center at the expense of the E'_{γ} spectra. Shown are (a) a 100 nm dry University oxide, (b) a 120 nm dry Sandia radiation soft oxide, (c) a 35 nm wet Harris (Cl) oxide containing Cl, (d) a 35 nm wet Harris (REOX) reoxidized oxide, and (e) an 850 nm Harris (no-Cl) oxide specially processed to eliminate Cl. In each case, approximately 5×10^{13} holes/cm² were injected.

create electron hole pairs.²⁷ The holes are driven across the oxide while electrons are swept out to remove corona charge. This process is repeated until the desired number of holes is injected. To inject electrons, we expose the positively corona charged oxides to $(hc/\lambda \leq 5 \text{ eV})$ ultraviolet (UV) photons. The $\leq 5 \text{ eV}$ UV photon exposure photoinjects electrons from the Si valence band into the SiO₂ conduction band; the electrons are driven across the oxide by the positive bias. The number of injected holes is determined by $C(\Delta V) = Q$, where *C* is the geometric capacitance of the oxide and ΔV is the difference between the pre- and post-illumination surface potential measurements.

Figure 1 displays ESR traces of a variety of conventionally processed thermally grown thin SiO₂ films on silicon after the injection of approximately 5×10^{13} cm². (Gains vary considerably so that the line shapes are clearly visible for samples with spin densities which differ by two orders of magnitude.) Traces (a)-(c) and (e) show that the hole injection results in the creation of an ESR signal with a zerocrossing g=2.0019 in four widely different, yet reasonably processed oxides. (Several years ago, a signal termed " E_{δ}' " was reported in thermal SiO_2 .⁵ Quite recently, a signal termed E'_{δ} was reported in thermal SiO₂ subjected to a similar VUV irradiation.^{18,19}) The signal at g=2.0019 has a very narrow (apparent width about 0.8 G) and apparently structureless line shape. Both the line shape and zero-crossing gof this signal most closely correspond to the E'_{δ} center first reported by Griscom and Friebele²⁰ in bulk fused silica.

Also present in traces 1(a)-(c), (e) are $E'_{\gamma p}$ centers at g=2.0005. The commonly observed $E'_{\gamma p}$ centers are present in equal or higher densities than the *EP* centers but because the spectrometer was optimized to detect the very narrow *EP*



FIG. 2. $E'_{\gamma p}$ and EP defect density vs hole injection fluence. (The lines are drawn only as a guide to the eye.)

signal and because very narrow signals show up very strongly,²⁸ the $E'_{\gamma p}$ signal shows up only weakly.

Although Griscom and Friebele²⁰ proposed structure for the E'_{δ} involves an unpaired electron delocalized in a cavity of Cl capped Si atoms, the strongest E'_{δ} -like trace (e) was observed on a Harris (no-Cl) oxide. Ten times weaker signals appear in oxides prepared in high Cl content environments. This result very strongly suggests that our defect is inconsistent with their model. It is for this reason we label the defect spectra EP (Provisional E' assignment). Recent observations¹⁷ also suggest that Cl is not involved at the E'_{δ} center site in SIMOX buried oxides.

EP density varies from 9×10^{11} /cm² in the Harris (no-Cl) and Sandia oxides to less than $10^{10}/\text{cm}^2$ in the Harris (REOX). The two orders of magnitude variation in EP defect density indicates that EP precursor density depends strongly on processing details. EP density is greatest in the thick Sandia and Harris (no-Cl) oxides and smallest in the thin Harris (Cl) oxides, suggesting a thickness dependence. A thickness dependence is consistent with the EP distribution. Etchback measurements on our thickest samples reveal that EP centers are distributed from near the Si/SiO₂ interface to deep into the oxide (200 nm), a distribution much broader than that of $E'_{\gamma p}$ centers in the same samples; $E'_{\gamma p}$ centers are mostly within 10 nm of the Si/SiO₂ interface. Trace 1(d) shows that the EP center density is below our detection limit in the Harris (REOX) reoxidized 35 nm wet oxide. This may be a result of reoxidation.²⁹ Vanheusden et al.¹⁷ also observed a similar precursor annihilation in reoxidized SIMOX buried oxides which they attributed to reoxidation. It is perhaps important to mention that these measurements were made within hours of the hole injection sequences. Simply storing the posthole injection samples for several days at room temperature and pressure in a normal atmosphere greatly reduces the EP signal amplitude.²⁹

In order to more quantitatively evaluate the possible technological significance of *EP* centers, especially in relation to $E'_{\gamma p}$ centers, we measured the approximate electron and hole capture cross sections of both centers. We utilized the Harris (no-Cl) samples since they exhibited quite strong *EP* and $E'_{\gamma p}$ signals. Figure 2 shows *EP* and $E'_{\gamma p}$ defect density versus hole injection fluence. From this plot, we calculate that the *EP* precursors have a much larger hole capture cross section ($\sigma \approx 10^{-13}$ cm²) than $E'_{\gamma p}$ centers ($\sigma \approx 10^{-14}$



FIG. 3. $E'_{\gamma p}$ and EP defect densities vs injected electron fluence after hole injection. (The lines are drawn only as a guide to the eye.)

cm²). *EP* density first saturates at low hole fluences and then decreases at higher hole fluences while $E'_{\gamma p}$ density does not saturate but continues to increase. It is not clear at this time why *EP* density decreases at higher hole fluences; one possibility is the instability of E'_{δ} centers at room temperature over the time frame of these measurements;²⁹ another is that the defect precursors could be trapping two holes.²⁰

Figure 3 illustrates remaining *EP* and $E'_{\gamma p}$ defect densities versus number of injected electrons. From this plot we calculate that the electron capture cross section of positively charged *EP* centers ($\sigma \approx 10^{-12}$ cm²) is also much larger than that of the $E'_{\gamma p}$ centers. $E'_{\gamma p}$ centers seem to have at least two distinct electron capture cross sections of $\sigma \approx 10^{-13}$ cm² and $\sigma \approx 10^{-14}$ cm². (The $E'_{\gamma p}$ result was noted in Ref. 7.)

Our observation of EP centers and identification of their charge trapping properties is somewhat surprising in view of earlier studies.^{1–8} Why have previous studies of charge trapping in gamma^{1-6,8} and VUV⁷ irradiated oxides not reported *EP* centers? (Our $E'_{\gamma p}$ centers are apparently the E' variant reported in other studies¹⁻⁸ of irradiated thermal SiO₂ films.) Several properties of the EP centers, their larger capture cross section for electrons than holes, their apparently broad distribution throughout the oxide, and their short term instability, all militate against their observation in an oxide x-ray or gamma irradiated under technologically meaningful conditions (positive gate bias during hours of irradiation). EP centers probably contribute to oxide space charge significantly only for conditions of low, relatively pure hole injection fluence such as hot hole injection. EP centers are probably not so important for X or gamma irradiation in which both electrons and holes are present throughout the oxides, especially if the irradiations take place over a period of many hours.

It is not so obvious why EP centers were apparently not detected in the earlier and quite similar study of charge trapping in VUV irradiated corona charged oxides by Warren *et al.*⁷ The fact that EP centers account for a significant fraction of the charge trapping in at least some of the oxides we studied combined with the fact that even very low EP defects densities are easily detectable makes the absence of EPsignals in the earlier Warren *et al.*⁷ study particularly surprising. Perhaps the dependence of defect precursor density on processing can explain this discrepancy.

The "zero order" picture of a single E' oxide charge

trapping center may be significantly incomplete. Our results indicate that a single E' precursor cannot explain all charge trapping in all thermal oxides. We have shown that EP $(E'_{\delta}$ -like) centers can occur in a fairly wide variety of thermal oxides. The density of EP centers in these oxides is strongly processing dependent. Positively charged EP centers, with their large electron and hole capture cross sections, could play a significant role in the charge trapping properties of thermal SiO₂ films under some circumstances.

We thank Harris Semiconductor, the Defense Nuclear Agency, and the Office of Naval Research for support.

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