

# Electron-spin-resonance evidence for an impurity-related $E'$ -like hole trapping defect in thermally grown $\text{SiO}_2$ on Si

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Using electron spin resonance (ESR), a new electrically active point defect in thermally grown  $\text{SiO}_2$  films on Si has been detected. The defect has a large capture cross section for electrons when it is paramagnetic and holes when it is diamagnetic (ESR inactive). The  $g$ -tensor values, symmetry, and microwave power saturation characteristics are all similar to those of the well-known  $E'$  family of amorphous  $\text{SiO}_2$  defect centers. © 1994 American Institute of Physics.

Thermally grown  $\text{SiO}_2$  pervades modern metal-oxide-semiconductor field-effect-transistor (MOSFET) microelectronic device structures. Charge in the oxide can be generated by ionizing radiation,<sup>1</sup> hot-carrier injection,<sup>2</sup> and high oxide fields.<sup>3</sup> Trapped gate oxide charge affects the characteristics of MOSFET transistors, creating threshold voltage shifts and, possibly, device failure.<sup>4</sup> For these reasons, charge trapping in thermal  $\text{SiO}_2$  on Si has been widely studied. In the early 1980s, an electron-spin-resonance (ESR) study at Sandia National Laboratories established a rough one-to-one correspondence between trapped oxide positive charge and  $E'$  centers in pristine (very clean) irradiated thermal  $\text{SiO}_2$  on Si.<sup>5-7</sup> ( $E'$  centers are unpaired electrons on silicons associated with oxygen vacancies.<sup>7,8</sup>) This work has been confirmed by many later ESR studies.<sup>9-13</sup> Until recently, little distinction was made regarding possible variations in  $E'$  structure or  $E'$  ESR spectra in thin films.

Recently, however, a number of new  $E'$ -like variants has been reported in (for the most part "exotic") thin films.<sup>14-25</sup> These include a "peculiar" line shape in separation by implanted oxygen (SIMOX) buried oxides,<sup>14,15</sup> the 74G doublet,<sup>9,16-18</sup> the 10.4G doublet,<sup>16,19</sup>  $EX$  center,<sup>20</sup> the  $EH$  center,<sup>21</sup>  $E'_\delta$ -like centers,<sup>22-24</sup> and the  $EP$  center.<sup>25</sup> (Some<sup>20-25</sup> of these spectra bear resemblance to an ESR spectrum reported by Griscom and Friebele in bulk fused silica which they linked to a chlorine impurity complex.<sup>26</sup>) Recent work by Conley *et al.*<sup>25</sup> demonstrated that at least two different  $E'$  variants could participate in charge trapping in a range of conventionally processed thermal oxides. Conley *et al.*<sup>25</sup> concluded that it is likely that the large electron capture cross section and long-term instability of the  $EP$  center could allow it to play a significant role in thermally grown oxides subjected to a low, pure hole injection fluence. They also confirmed that the (so called)  $E'_\gamma$  center that has dominated most earlier ESR studies of thin-film thermal

$\text{SiO}_2$  is likely to dominate charge trapping in cases of irradiation under positive gate bias.

In this communication, we identify another electrically active defect in thermally grown  $\text{SiO}_2$  on Si which, to the best of our knowledge, has not previously been observed in thin oxide films. Using ESR measurements in combination with oxide charge injection [via vacuum ultraviolet (VUV) and ultraviolet (UV) illumination with corona ion biasing], we find that this paramagnetic (ESR active) defect captures electrons and that its diamagnetic (ESR inactive) precursor captures holes, in both cases with large capture cross sections. The  $g$  tensor and microwave power saturation characteristics of the defect suggest that it is likely to be a member of the  $E'$  family of defects, possibly decorated by an impurity.

The oxides used in this study were grown on lightly doped ( $\rho \sim 100 \Omega \text{ cm}$ ) (111)  $n$ -type Czochralski Si substrates at the Harris Semiconductor facility at Findlay, Ohio. They 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 70 nm at 800 °C in an ambient with an  $\text{O}_2$  flow rate of 3250 sccm, a  $\text{H}_2$  flow rate of 3500 sccm, and a TCA flow rate of 50 sccm. After oxidation, they were annealed for 20 min in  $\text{N}_2$  at 1050 °C and exposed to an 800 °C reoxidation step. The oxides are suspected to suffer from microcontamination.

ESR measurements were performed at room temperature on a Bruker Instruments  $X$ -band spectrometer. Spin densities and zero crossing  $g$  values ( $g = h\nu/\beta H$ ) were determined using a  $\text{TE}_{104}$  double resonant cavity and a calibrated "weak pitch" spin standard. Relative spin densities are accurate to  $\pm 10\%$  while absolute numbers are accurate to within a factor of 2. Defect profiles were determined with a series of oxide etchbacks and ESR measurements. The etchant used was a

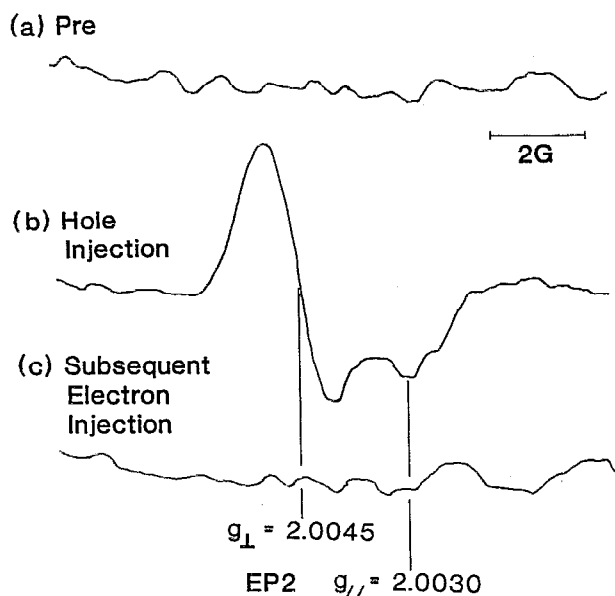


FIG. 1. ESR traces of Harris oxides: (a) precharge injection; (b) postinjection of  $6 \times 10^{13}$  holes/cm<sup>2</sup>; and (c) after subsequent injection of  $6 \times 10^{13}$  electrons/cm<sup>2</sup>. Spectrometer settings are optimized for detection of the EP2 spectra. Note the appearance and disappearance of the lineshape at zero-crossing  $g = 2.0046$ .

buffered HF acid solution; oxide thickness was measured using a Sagax 125E ellipsometer.

We flooded oxides with holes by applying positive bias to the oxide surfaces with corona ions<sup>27,28</sup> and then exposing the oxide surfaces to 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 create electron hole pairs.<sup>29</sup> The holes are driven across the oxide while electrons are swept out to remove positive corona charge. To inject electrons, we exposed positively corona charged oxides to UV photons ( $hc/\lambda \leq 5$  eV). The UV photon exposure photoinjects electrons from the Si valence band into the SiO<sub>2</sub> conduction band; the electrons are driven across the oxide by the positive bias. In both cases the number of injected charges  $Q$  is determined from  $C(\Delta V) = Q$ , where  $C$  is the geometric capacitance of the oxide and  $\Delta V$  is the difference between the pre- and post-illumination Kelvin probe measurements.

Figure 1(b) shows that hole injection (approximately  $6 \times 10^{13}$  holes/cm<sup>2</sup>) generates an ESR active signal (approximately  $3 \times 10^{11}$  defects/cm<sup>2</sup>) at a zero crossing  $g = 2.0045$ . No other signals in the range of  $g = 2.00$  are visible. Neither  $E'_\gamma$  ( $g = 2.0005$ ) centers nor  $EP$  ( $g = 2.0019$ ) centers are generated in these oxides. We refer to this defect as EP2 for reasons discussed later. The hole injection also qualitatively results in a negative shift in quasistatic  $C$ - $V$  curves. In Fig. 1(a) it is seen that no signals could be detected (detection limit  $5 \times 10^{10}$ /cm<sup>2</sup>) in the oxides prior to hole injection. Since the EP2 signal is generated by hole injection, it is likely that the EP2 centers are trapped holes. In order to more convincingly establish whether the EP2 defects are positively

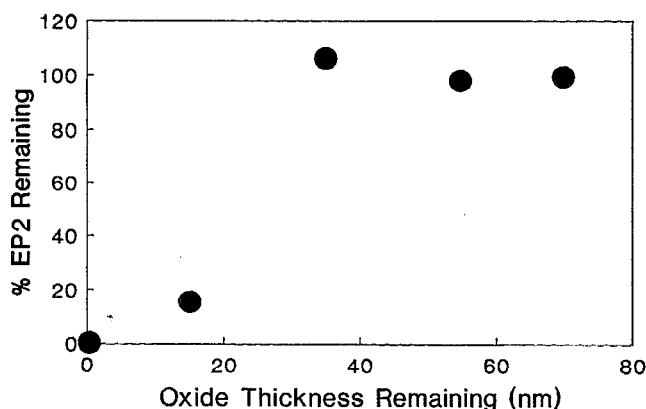


FIG. 2. EP2 defect density vs remaining oxide thickness.

charged when paramagnetic, we subsequently injected electrons into the oxides.

Figure 1(c) shows that injection of approximately  $6 \times 10^{13}$  electrons/cm<sup>2</sup> subsequent to hole injection completely annihilates the EP2 defect centers. The fact that the EP2 defect centers have a large capture cross section for electrons when paramagnetic and holes when diamagnetic (in both cases  $\sigma > 10^{-14}$  cm<sup>2</sup>) very strongly indicates that EP2 centers are electrically active and positively charged when paramagnetic.

The spatial distribution of electrically active defects is important in determining their potential to affect device reliability. The closer the defect is to the Si/SiO<sub>2</sub> interface, the more pronounced effect it can have on device characteristics. By performing ESR measurements on samples with oxide surfaces either positively (+17 V) or negatively (−17 V) charged via corona ions, we found that the paramagnetism and thus presumably the charge state of the EP2 defect is not affected by Si band bending. Since Si/SiO<sub>2</sub> interface traps are affected by band bending, EP2 centers are ruled out as interface traps. Next, in a series of steps, we etched back the oxide with a buffered HF solution and performed ESR measurements at each step. The results of this rough etchback are displayed in Fig. 2. The EP2 centers are spatially distributed in the oxide between roughly 10 and 35 nm from the Si/SiO<sub>2</sub> interface in a 70-nm-thick oxide. In addition, the spectrum is magnetic-field-orientation independent, as is expected from its presence in an amorphous solid.<sup>30</sup>

A number of considerations are involved in identifying the structure of a paramagnetic defect. Hyperfine interaction with a magnetic nucleus such as <sup>17</sup>O or <sup>29</sup>Si is generally very useful in determining structure.<sup>8,30</sup> Although our modest signal-to-noise ratio precludes observation of the <sup>29</sup>Si nuclei hyperfine spectra, other information such as symmetry, the ESR spectrum's power saturation characteristics, processing data, and previous work allows us to draw conclusions about the EP2 center's chemistry. As seen in Fig. 1(b), the defect has a powder pattern lineshape characteristic of axial symmetry with  $g_{\parallel} \approx 2.0030$  and  $g_{\perp} \approx 2.0045$ . The EP2 ESR signal saturates at low (tens of  $\mu$ W) levels of microwave power. Low power saturation, and axial symmetry, with both  $g_{\parallel}$  and  $g_{\perp}$  values near the free electron  $g = 2.0023$ , are all character-

istics of  $E'$  centers.<sup>5-8,31-33</sup> Thus, it is not unreasonable to provisionally assume that this defect is a member of the  $E'$  family of defects. [It is for these reasons that we label the defect  $EP2$ , the  $E$  for  $E'$ , the  $P$  for provisional, and the 2 to distinguish this defect from the  $EP$  (provisional  $E'$ ).<sup>25</sup>]

In addition, the oxides in which we observe the  $EP2$  center defects are from a processing line known to exhibit device instability problems, possibly related to microcontamination. An ESR spectrum similar to the  $EP2$ , although less well resolved, was reported in bulk samples of significant alkali content silicate glass by Schreurs.<sup>31</sup> He attributed the spectrum to the Weeks<sup>32</sup>  $E'_1$  center. Later, Cases and Griscom<sup>33</sup> observed a similar but better-resolved spectrum ( $g_{\parallel}=2.0017$ ,  $g_{\perp}=2.004$ ), also in bulk samples of significant alkali content silicate glass. They attributed the spectrum to an alkali-impurity-related  $E'$  center. On the basis of our observations of lineshape and spin lattice relaxation times and a comparison of this data to earlier observations of Schreurs<sup>31</sup> and Cases and Griscom,<sup>33</sup> we suggest that the  $EP2$  is an  $E'$ -like variant, an unpaired electron on an oxygen-deficient Si, which is somehow related to a microcontaminant impurity. The low  $g$  anisotropy indicates low-spin-orbit coupling,<sup>30</sup> suggesting either that the unpaired electron spends most of its time on the Si or that impurity is not a large atom. It is known that defects in Si getter impurities,<sup>34</sup> and it was mentioned that we do not detect the ubiquitous  $E'_\gamma$  centers in the same oxides as  $EP2$  centers. This suggests that the  $E'_\gamma$  sites may be gettering the impurities, resulting in the observed  $EP2$  spectra. This is a *provisional* identification, of course, and awaits further experimental characterization for confirmation.

In summary, we have identified a new electrically active defect in conventional thermally grown  $\text{SiO}_2$  on Si. The defect captures electrons when paramagnetic and holes when diamagnetic with large capture cross sections and is distributed 10–35 nm from the Si/ $\text{SiO}_2$  interface. This defect has axial symmetry, low  $g$  anisotropy, and saturates at low levels of microwave power. These combined properties suggest it is an  $E'$  variant. Since we observe the center in an oxide that may possibly be microcontaminated and since similar spectra in bulk oxides have been linked to impurity-related  $E'$  centers,<sup>31,33</sup> we provisionally associate the spectrum with an  $E'$  impurity defect. The fact that these defects have been detected in oxides processed in a commercial semiconductor fab suggests that this defect could be a device reliability concern under some circumstances. This study demonstrates the potential power of ESR as a tool to study fab line problems with conventionally processed thermal  $\text{SiO}_2$  on Si.

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