

Room temperature reactions involving silicon dangling bond centers and molecular hydrogen in amorphous SiO₂ thin films on silicon

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Exposing thin films of amorphous SiO₂ to molecular hydrogen at room temperature converts some silicon dangling bond defects, *E'* centers, into two hydrogen coupled complexes. These reactions may play important roles in radiation and hot carrier instabilities in metal/oxide/silicon devices.

When metal/oxide/silicon (MOS) devices are subjected to ionizing radiation, hot carrier damage, or any process in which charge carriers are present in the oxide, interface states are created at the Si/SiO₂ interface.¹⁻⁹ The presence of holes in the oxide is most effective in triggering the interface state generation process.^{8,9} Studies of the transient response of irradiated devices shows that most of the damage occurs in seconds to minutes after irradiation at room temperature.⁴⁻⁶

Early studies of MOS radiation damage showed that the radiation tolerance of the devices was strongly affected by hydrogen in high-temperature processing steps.¹⁻³ Studies of the interface state creation process⁴⁻⁶ have been interpreted by McLean.¹⁰ In McLean's model,¹⁰ holes interact with the oxide to liberate a hydrogen species which then drifts to the Si/SiO₂ interface. At the interface, the hydrogen reacts to form silicon dangling bond interface state defects. The McLean model is clearly consistent with many experimental results.^{4-6,11,12}

Recent evidence suggests that *molecular* hydrogen may play a significant role in the radiation damage process. For example, the density of radiation induced interface states can be significantly enhanced by placing irradiated MOS devices in an ambient rich in molecular hydrogen.¹³⁻¹⁵

Although experimental evidence regarding hydrogen's role in the radiation damage process is fairly compelling, it consists almost entirely of electronic measurements. There is little direct experimental evidence regarding the atomic scale structures involved in reactions of hydrogen and radiation damage centers in the silicon dioxide films on silicon. Reactions of particular interest would obviously involve SiO₂ hole trap sites and hydrogen and would proceed in a period of seconds to minutes at room temperature.

In this letter we report evidence for several reactions involving *E'* centers and hydrogen which take place when SiO₂ films are exposed to hydrogen at room temperature. (The *E'* center is an unpaired electron residing in an *sp* hybridized orbital of a silicon bonded to three oxygens;¹⁶ in thermal oxides in *E'* is a hole trapped in an oxygen vacancy.¹⁷) These reactions take place within minutes after our very thick (≈ 4800 Å) oxide films are exposed to hydrogen. We think that these reactions may play a part in the MOS interface state radiation damage process for several reasons. (1) The *E'* center is the dominant deep hole

trap in MOS oxides;¹⁷ (2) the reactions take place in a time scale which is of the correct order of magnitude expected in the damage process; (3) it is known that, or at least strongly suspected that, molecular hydrogen is present in irradiated MOS oxides;¹⁸ (4) recent studies suggest that the radiation damage at the Si/SiO₂ interface may be triggered by a reaction involving hydrogen at the hole capture site.¹⁹

Our study involves room temperature electron spin resonance (ESR) measurements of SIMOX (separation by implantation of oxygen) buried oxides. The 4800 Å thick SIMOX buried oxides utilized in this study were prepared by implanting 1.8×10^{18} oxygens/cm² at an energy of 200 keV. The ion current density during deposition was 34 mA/cm². The temperature of the substrate during implantation was 640 °C. The implant step was followed by a 5 h anneal at 1315 °C in an ambient of 99.5% Ar and 0.5% O₂. The silicon surface orientation was (100); the silicon is *n*-type with a resistivity of about 30 Ω cm. A residual oxide layer formed by the high-temperature anneal, as well as the top silicon layer, were removed by etches in HF (oxide) and KOH (silicon) prior to the study. The etches were carried out at room temperature. After etching, the samples were cut into 3.5 mm \times 20 mm rectangles and, with the oxides protected, were subjected to a buffered HF etch at room temperature. This last etch removes mechanical edge damage.

Earlier, we demonstrated that SIMOX buried oxides exhibit an extremely high ($\sim 10^{18}$ /cm³) density of *E'* precursors.^{20,21} The density of *E'* precursors is higher than that observed in thermal thin films. This increased *E'* density makes it possible to observe several otherwise difficult to observe hydrogen *E'* complexes. Although these oxides are not identical to the thermal SiO₂ films of MOS gate oxides, the reactions observed here are also likely to take place at some sites in thermal oxides.

We subjected the Si/SiO₂ samples to ~ 40 h of vacuum ultraviolet ($hc/\lambda < 10.2$ eV) irradiation from a deuterium lamp at room temperature. (A second set of samples were exposed to 210 Mrad of gamma irradiation from a Co⁶⁰ source. These gamma irradiated samples were not subjected to the KOH etch; they retained the ~ 1 μm silicon overlayer. The gamma irradiated samples and the VUV irradiated samples exhibit nearly identical ESR spectra.) A post-VUV irradiation trace is illustrated in Fig. 1(a). A

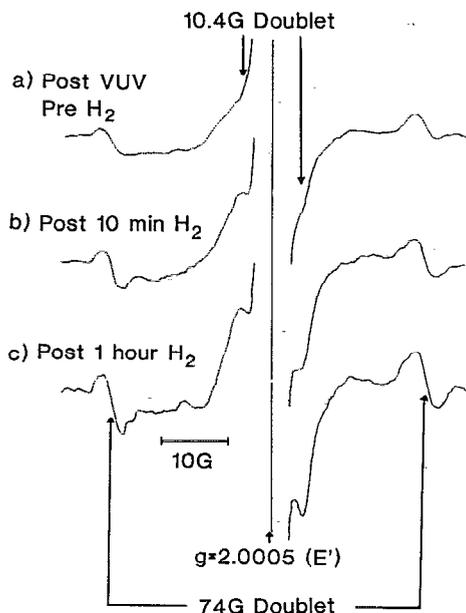


FIG. 1. Trace (a) illustrates ESR data from a SIMOX oxide sample after exposure to VUV illumination. The large central line corresponds to the ordinary E' defect. Trace; (b) illustrates a trace after the sample was exposed to 10 min of exposure to a 10% H_2 ambient; Trace (c) illustrates the trace after 1 h exposure to H_2 . An additional hour of exposure did not significantly alter the spectra.

very strong signal appears at a zero crossing $g=2.0005$ and a weak doublet signal appears with a separation of 74 G. The strong center line is due to ordinary E' centers illustrated in Fig. 2(a); the weak doublet spectra is due to an E' center in which the paramagnetic silicon is bonded to two oxygens and a hydrogen atom; its structure is illustrated in Fig. 2(b).^{22,23} The weak doublet spectra comprises 3%–5% of the total E' spins.

In Figs. 1(b) and 1(c) we illustrate ESR traces taken on the same samples of Fig. 1(a), but after 10 min 1(b)

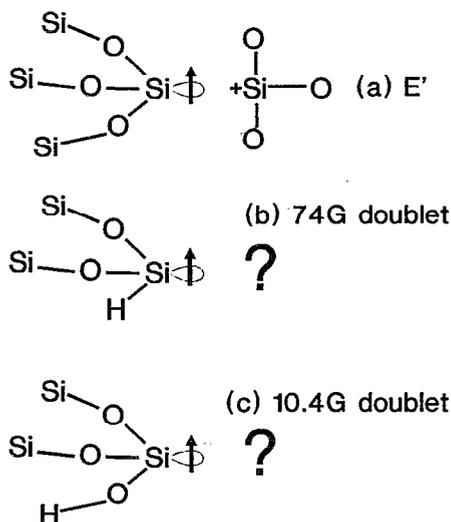


FIG. 2. This figure schematically illustrates the structure of (a) ordinary E' centers, (b) 74 G doublet centers, and (c) 10.4 G doublet centers.

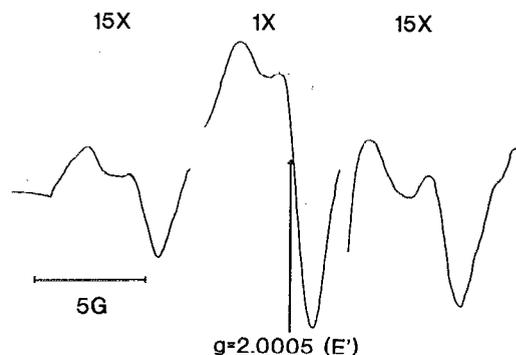


FIG. 3. This figure illustrates the 10.4 G spectrum with the spectrometer settings optimized to yield a relatively accurate line shape for the 10.4 G doublet lines.

and 1 h 1(c) exposure to (10% H_2 /90% N_2) forming gas at room temperature and atmospheric pressure. Note the large increase in the doublet spectra at 74 G separation and the appearance of two bumps on the center line with a separation of about 10.4 G. The 10.4 G doublet spectra is due to the hydrogen complex defect illustrated in Fig. 2(c).²³ The original E' line amplitude decreases by 25%–30% during the 1 h H_2 exposure; most of the change occurs in the first 10 min. While most of the 10.4 G change also takes place within 10 min, only about 30% of the 74 G change takes place within that time. The number of defects associated with the sum of the newly created 10.4 and 74 G doublet signals are approximately equal to the 25% decrease in initial E' amplitude. (The total number of spins is preserved.) We thus tentatively conclude that we are observing a transformation of standard E' centers Fig. 2(a) into two hydrogen complexed E' centers [Figs. 2(b) and 2(c)]. The process occurs in a period roughly equal to the time required for molecular hydrogen to diffuse across the oxide.¹⁸

Figure 3 illustrates an ESR trace with spectrometer settings optimized to accurately illustrate the 10.4 G doublet line shapes. The line shapes are what one would expect from the structure of Fig. 1(c);²³ however, the doublet splitting is slightly greater than 10.4 G.

Triplett, Takahashi, and co-workers^{24,25} were first to observe E' /hydrogen complexes in thin SiO_2 films on silicon. They subjected thermally grown oxides to very heavy irradiation ($\sim 2 \times 10^{10}$ rad) and then briefly exposed the oxides to 10% H_2 /90% N_2 forming gas at 110 °C. They noted a substantial decrease in the central E' line and the appearance of the 74 G doublet signal corresponding to a density which closely matched the decrease in the central E' intensity. The Triplett–Takahashi study noted that a 1 min exposure to UV illumination from a 250 W mercury lamp annihilated the 74 G doublet signal and slightly increased the central E' signal; the UV illumination resulted in a loss of oxide space charge which closely corresponded to the net change in the sum of E' and 74 G doublet defects. (The original positive charge density in the oxides closely matched the initial E' density.)

We also subjected the VUV irradiated/hydrogen soaked oxides to a brief (~ 4 min) exposure of UV illumi-

nation ($hc/\lambda \leq 5$ eV) from a mercury-xenon lamp. We found, as did Triplett and Takahashi, that the brief exposure annihilated the 74 G doublet signal and resulted in a modest increase in the ordinary E' signal. In addition, we found that this illumination reduced the 10.4 G signal amplitude by about 25%.

To further assess the electronic properties of the three E' defects we exposed the oxides to both penetrating UV and notch filtered, nonpenetrating VUV illumination ($hc/\lambda \approx 10.2$ eV) with bias applied across the oxides during the illumination. The bias was applied with either positive or negative corona discharge ions; the corona ion potential was measured with a Kelvin probe electrostatic voltmeter.

We first UV irradiated ($hc/\lambda \leq 5$ eV) the oxides under positive oxide bias (oxide field ~ 1 – 3 MV/cm) to photoinject electrons from the silicon into the oxide. The photoinjection of approximately 5×10^{13} electrons/cm² resulted in a near-complete annihilation of the 74 G signal (this also occurred with the unbiased UV illumination) but the ordinary E' signal increased by an amount (+35% vs +20%) significantly larger than was observed in the unbiased UV illumination. The 10.4 G doublet signal was reduced by $\approx 50\%$ during the process.

We also subjected oxides to UV illumination under negative oxide bias. The negative bias (oxide field ~ 1 – 3 MV/cm) should substantially impede electron photoinjection. We found that this negative bias illumination also completely eliminated the 74 G signal, substantially reduced ($\approx 50\%$) the 10.4 G signal, but did *not* change the central E' amplitude.

The results of our positive, negative, and zero bias UV illuminations suggest that the central E' signal increases are result of electron photoinjection into the oxide. In addition, these results strongly suggest that both the 10.4 and 74 G signals are responding directly to the UV photons.

In order to evaluate these conclusions we injected electrons and holes into the oxides without exposing the oxide bulk to ultraviolet photons. We did this by charging the oxide surfaces with corona ions and then exposing the oxides to vacuum ultraviolet ($hc/\lambda \approx 10.2$ eV) light from a notch filtered deuterium lamp. The oxide's optical absorption coefficient is extremely large for photons of this energy $\sim 10^6$ /cm; thus virtually all the photons are absorbed in the top 100 Å of the 4800 Å oxide. The photons create electron hole pairs in the top ≈ 100 Å of the oxide and thus positive corona bias floods the bulk of the oxide with holes; negative corona bias floods the bulk of the oxide with electrons. In both cases the fluence of injected charge carriers was about 5×10^{13} /cm² and the average oxide field during the process was ~ 1 – 3 MV/cm. We found that when electrons were injected into the oxide the simple E' amplitude was substantially increased ($\approx +35\%$), but we observed little change in the 10.4 or 74 G doublet signals. Injecting holes into the oxide also resulted in a substantial ($\approx +35\%$) increase in the simple E' and also did not

significantly change either the 74 or 10.4 G doublet amplitude.

The results of the VUV illumination measurements strongly suggest that the changes observed in the 10.4 and 74 G signals with UV illumination are due to photons interacting with the defects. The results also suggest strongly that the E' signal can be increased by electron capture at previously diamagnetic sites. This does not appear to happen in SIMOX oxides which have not been exposed to hydrogen.^{20,21} These new results strongly suggest that the E' /hydrogen reactions involve substantial structural changes at the E' site. Our results also suggest that the hydrogen exposure can result in the creation of neutral paramagnetic single silicon dangling bond sites from sites which had initially been holes trapped at oxygen vacancies.

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