Experimental evidence for two fundamentally different E' precursors in amorphous silicon dioxide

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E' centers (trivalent silicons) in two silicate systems, thermally grown SiO_2 films on silicon and high surface area bulk sol–gel silicates, have been investigated. In the thermally grown silicon dioxide films, earlier work is extended by demonstrating that the hole trapping process is reversible; no complex structural rearrangement occurs at the hole trapping site (E' centers) after subsequent electron capture. This provides further evidence that these thermal oxide E' centers are oxygen vacancies as originally proposed by Feigl, Fowler and Yip. Also investigated is the radiation-induced generation of paramagnetic centers in high surface area sol–gel silicates containing various concentrations of the Raman active 608 cm^{-1} D_2 band attributed to strained cyclic trisiloxanes (three-membered rings). The results suggest a correlation between the concentration of the strained three-membered rings and the concentration of radiation-induced E' and paramagnetic oxygen centers, thus providing the first substantive evidence of the relationship between a *specific strained siloxane structure* and radiation damage in amorphous silicon dioxide. These results suggest the existence for (1) two different fundamental E' precursors and (2) a relationship between atomic level stress and the radiation damage process in amorphous silicon dioxide.

1. Introduction

The effects of ionizing radiation on amorphous silicon dioxide have been extensively investigated for over thirty years [1–6]. Ionizing radiation degrades the insulating layers of metal oxide semiconductor field effect transistors (MOSFETs) [4–6] and impairs the transmission properties of low loss optical fibers [7,8]. Thus, a detailed understanding of the mechanisms and structural origins of the radiation damage process in amorphous silicon dioxide (a-SiO_2) is of considerable interest.

Electron spin resonance (ESR) is generally recognized as a sensitive probe of atomic scale defect structure in a-SiO_2. Extensive ESR studies have been performed on crystalline quartz [2,9] and bulk a-SiO_2 [7,8,10] subjected to various forms of irradiation (X-rays, gamma rays and neutrons). These investigations have identified several intrinsic point defects: E' centers, peroxy radicals and non-bridging oxygen hole centers (NBOHC). The E' center is an unpaired electron on a silicon bonded to three oxygen atoms [9,10]; it is the most extensively investigated point defect in a-SiO_2. One theoretical model [11–14] identifies the E' center precursor as an oxygen vacancy ($O_3 \equiv Si–Si \equiv O_3$). The positive charge state of the oxygen vacancy E' centers in gamma irradiated and vacuum ultraviolet irradiated thermally grown

silicon dioxide films on silicon was experimentally established by a number of workers [15–22].

The peroxy radical ($\cdot$O–O–Si$\equiv$O₃) and NBOHC ($\cdot$O–Si$\equiv$O₃) have been identified as two intrinsic paramagnetic oxygen centers that predominate in 'dry' (low water, < 5 ppm OH) and 'wet' (high water) silicas, respectively [7,23–25]. The precursors for the peroxy radical and NBOHC are believed to be an oxygen surplus site (O₃$\equiv$Si–O–O–Si$\equiv$O₃) [23] and a hydroxyl site (O₃$\equiv$SiO–H) [24], respectively.

Unfortunately, ESR does not always provide information concerning precursor structures of defects since they may be diamagnetic. Other experimental tools in conjunction with ESR are usually needed to obtain information regarding the nature of a defect's precursors [2,26,27]. In this investigation, we have investigated E′ centers in two amorphous silica systems – thermally grown silicon dioxide films on silicon and high surface area bulk silicate gels; we find evidence for two fundamentally different E′ precursors: (1) oxygen vacancies and (2) structures involving strained silicon–oxygen bonds. To obtain this information, ESR in conjunction with other experimental techniques were used.

First, we further investigate the hole trapping process in thermal oxides on silicon using ESR, capacitance vs. voltage (CV) measurements and a series of electron and hole injection sequences. Examining the dynamic behavior of E′ centers [28], we find that the E′ center can be cycled back and forth repeatedly from positively charged to neutral to positively charged without detectably altering the ESR signature. This result, we believe, is completely consistent with the theoretical model of the E′ center proposed by Feigl, Fowler and Yip (FFY), the oxygen vacancy model [11–14].

Second, we investigated the generation of paramagnetic centers in high surface area sol–gel silicates. Based on the results of ESR, Raman scattering, and ²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR) experiments, we present evidence for a new fundamental E′ and oxygen hole center (unpaired spin on an oxygen atom) precursor involving strained silicon–oxygen bonds. For years it has been sug-

gested that atomic level stress plays a role in the radiation induced damage process in a-SiO₂ [29–32]. Devine and Arndt [31,32] have provided the first experimental evidence that this is the case by observing large enhancements of defect concentrations in plastically densified silicates over undensified ones. No relationship has been established between paramagnetic point defects generated by ionizing radiation and a *specific* strained silicate structure to our knowledge. This study provides evidence that suggests that strained cyclic trisiloxanes (three-membered rings – an *n*-membered ring has *n* silicon tetrahedra connected by *n* bridging oxygens) are also precursors to E′ centers as well as oxygen hole centers (OHC).

We have used Raman scattering combined with earlier ²⁹Si MAS-NMR studies [33] to identify these strained silicate structures. The Raman vibrational band of interest in this study is the 608 cm^{-1} D₂ band. A model consistent with the data for this D₂ line is oxygen ring breathing vibrations of highly regular, planar, strained, cyclotrisiloxanes (three-membered rings) with Si–O–Si angles $\phi = 137°$ [33–39]. Molecular orbital calculations of three-membered ring structures indicate that the reduction of the Si–O–Si bond angle, ϕ, is accompanied by a reduction in the tetrahedral angle (from 109.5° to 103°) and an increase in the Si–O bond length (from 1.626 to 1.646 Å) [38]. By contrast, the average structure of amorphous silicon dioxide is believed to consist mainly of puckered, unstrained, 5–8-membered rings with average $\phi = 149°$ [40,41]. However diffraction studies clearly indicate that regular a-SiO₂ does contain a wide range of Si–O–Si intertetrahedral bond angles [42]. Bond angle (energy) calculations [43,44] indicate that strained bonds also exist in regular vitreous silica due to a distribution of bond angles around 149°. It may be the strained sites in regular forms of silica are also precursor sites to radiation induced paramagnetic defects.

We chose to investigate the radiation effects on high surface area gels since they exhibit the largest concentration of strained rings and are, thus, an ideal system to investigate the response of strained silicate species to ionizing radiation. However, we believe that our observations are

relevant to other high surface area silicates and to a wide range of fused silicas since the Raman D_2 band is present in all known forms of a-SiO$_2$, i.e., leached alkali silicate glasses, conventional fused silica, flame pyrolyzed SiCl$_4$ (e.g., Cab-O-Sil®), optical fibers and chemical vapor deposited dielectrics on Si. Essentially, all of the experimental features of the D_2 band in the silica gels are identical to those found in other forms of a-SiO$_2$; the only difference is that the concentrations of these rings in the high surface area dehydroxylated gels are significantly larger, because the formation of three-membered rings appears to be the preferable way to terminate the dehydroxylated silica surface [45].

Examining the high surface area silica gels simply enables us to study the relationship between the strained rings and the corresponding point defects generated in a more straightforward manner; by contrast, this would be extremely difficult in other forms of a-SiO$_2$ where the concentrations of these rings are so much smaller, that other radiation damage paramagnetic center precursors will most likely dominant.

First, we discuss our thermal oxide results that further demonstrate the E' precursor to be consistent with the oxygen vacancy model of FFY. Then, we present our results on the silicate gels that suggest that the E' precursor can also be a strained cyclic trisiloxane.

2. Experimental details – thermal oxide structures

The thermal oxides used in this study were steam grown at 1050°C on p-type (100 Ω cm) silicon with a (111) surface orientation. The oxide thickness was measured to be 1200 Å by ellipsometry, and the Si substrate thickness was 20 mils. The ESR measurements were made using a TE$_{104}$ double resonant cavity; a weak pitch standard was used to calculate the concentration of E' centers. When making ESR measurements, care was taken to avoid microwave cavity loading by aligning the samples in the cavity with the c-Si (111) interface plane perpendicular to the external magnetic field (this aligns the sample con-

jointly with the microwave magnetic field). Using fairly resistive Si substrates, and only two (4.0 × 20 mm) wafer slices also helped avoid microwave cavity loading. CV measurements (1 MHz) were made using a Boonton capacitance bridge and a Hg probe. The mid-gap shifts in the CV curves were used to calculate the number of holes trapped (or annihilated). By comparing the number of E' centers and the amount of space charge in the oxide (CV), the charge state of the E' center can be determined. We estimate that the absolute spin concentrations are accurate to at least a factor of two, the relative spin concentrations are accurate to about 10%.

To flood the oxide selectively with holes, we exposed it to vacuum ultraviolet (VUV) photons. The bare oxide structures were first exposed to positive corona ions [46] which applied a relatively ($\pm$15%) uniform potential of +25 V across the oxide. The samples were then placed in a vacuum (10^{-4} Torr) and exposed to 10.2 eV photons from a 50 W deuterium lamp. Since the bandgap of SiO$_2$ is about 9 eV, these photons create electron/hole pairs in the top 100 Å or so of the oxide. Under the action of a positive 'gate' bias, the holes are driven to the Si/SiO$_2$ interface; the electrons simply recombine with the positively charged corona ions. This procedure was repeated five times to increase our signal to noise ratio. Etch back experiments indicate that the positive charge is located near the Si/SiO$_2$ interface in accord with earlier works [17,47].

To flood the oxide selectively with electrons unbiased oxide structures were subjected to less energetic photons (< 5.5 eV photons) from a 100 W mercury lamp. This ultraviolet (UV) illumination photoemits electrons from the silicon valence band into the silicon dioxide conduction band.

3. Oxygen vacancy E' centers

The results of our multiple cycling of electrons and holes into thermal oxide structures are illustrated in figs. 1 and 2. In fig. 1, we illustrate our CV and ESR measurements of thermal oxides subjected to hole and electron injection sequences. Figure 2 shows the concentrations of E'

centers and space charge in the oxide as a function of illumination (injection) history. In fig. 1(a), we show the virgin CV and ESR measurements. Next the samples were flooded with holes as described earlier. As seen by the negative shift in the CV curve of fig. 1(b), hole trapping has occurred. From the ESR measurements (figs. 1(b) and 2), E' centers were also created. The concentration of E' centers is located close to the Si/SiO₂ interface as observed in earlier studies [15–18]. The E' center is identified by its double humped lineshape and zero-crossing $g = 2.0005$. The g factor is defined as $g = h\nu/\beta H$, where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton and H is the magnetic field at which resonance occurs.

Next, the samples were subjected to UV illumination (the oxide was flooded with electrons). After about 10 h of electron injection, we again

Fig. 2. Densities of trapped holes and E' centers in a thermal oxide subjected to various electron and hole injection sequences. The absolute error in the spin resonance measurements is a factor of two and relative error is about 10%. The estimated error in the concentration of trapped charge is 10%.
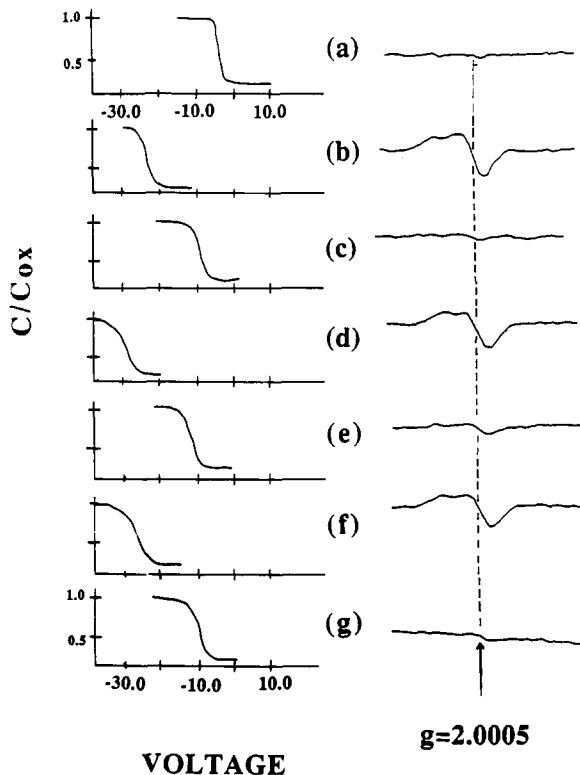
Fig. 1. CV curves and ESR traces for various electron and hole injection sequences: (a) virgin, (b) hole injection, (c) electron injection, (d) hole injection, (e) electron injection, (f) hole injection, and (g) electron injection.
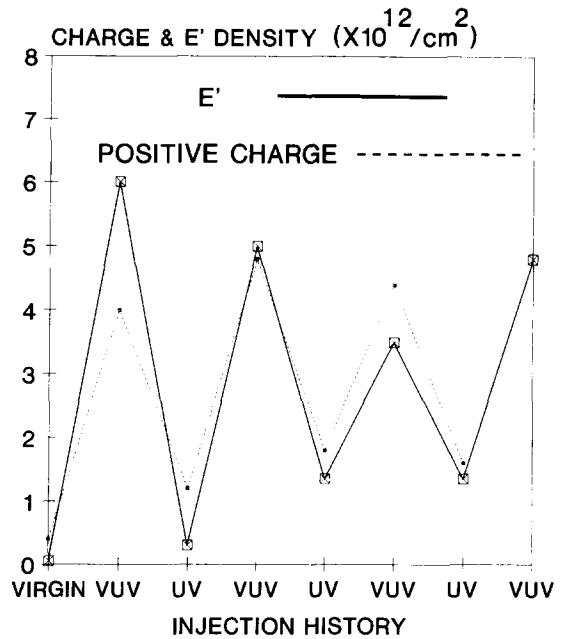
made CV and ESR measurements (figs. 1(c) and 2). We find that most of the E' centers and trapped holes have been annihilated.

At this point the cycling behavior of the E' center was investigated, i.e., we subject the samples to exactly the same hole and electron flooding procedure used in the first steps of the experiment. Our results are consistent with the oxygen vacancy model for the E' center [11–14]. The oxygen vacancy model of FFY is illustrated in fig. 3. Upon hole capture, an asymmetric relaxation occurs. In their model the unpaired electron is localized at one of the silicon sites, rather than shared by both. The other silicon is positively charged and decreases its energy by relaxing, approximately, into the plane of its three remaining oxygen neighbors, forming sp² hybrids. The FFY model agrees quite well with the ²⁹Si E' hyperfine data of Silsbee [9] in quartz and Griscom et al. [10] in bulk amorphous silica; these hyperfine studies showed that the unpaired elec-

tron is highly localized on one silicon atom. (However, as we shall show, this is not an unambiguous identification of precursor structure.) The positive charge state of the oxygen vacancy E' center was established by others on thin thermal oxide films [15–19,21,22]; this state is also consistent with this work.

After trapping the hole, the positively charged E' centers are a Coulombically attractive trap for electrons. We would expect that with electron injection into the oxide, these positively charged centers would readily capture the electrons, 'reforming' the neutral oxygen vacancy as illustrated in fig. 3 (bottom part). As shown in fig. 1(c), this is consistent with our observations.

Now, if the neutral oxygen vacancy is truly reformed, then upon hole injection we should again observe the generation of E' centers and positive charge. As illustrated in fig. 1(d), again this sequence is observed.

It is possible that the variation in the E' concentration following each hole flooding sequence (fig. 2) most likely results from the nature of the corona ions. The corona ion bias can vary by ±15% during each VUV illumination, which will vary the concentration of holes injected into the oxide by ±15%. (The procedure was repeated five times for each datapoint.) With a varying hole flux, the E' density may vary.

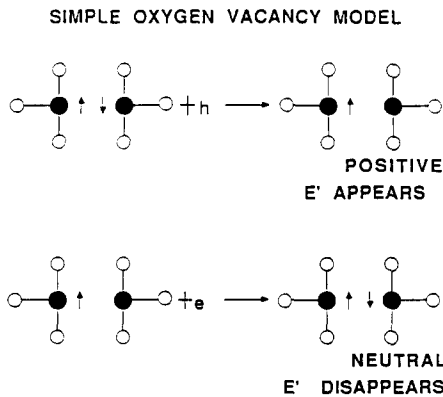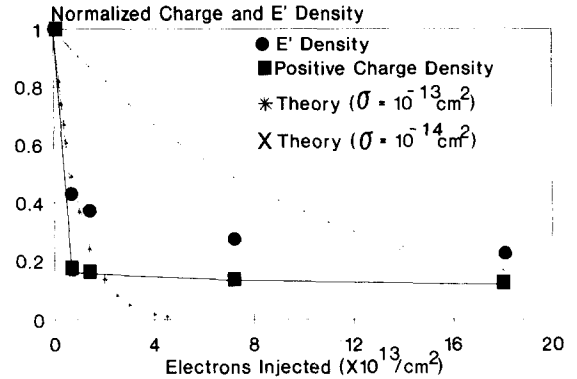In order to further demonstrate that the E' center is positively charged when paramagnetic,

Fig. 4. Decay of the E' center and the positive charge vs. the areal concentration of electrons photoinjected. The theoretical decay rate for defects with capture cross-sections of 1×10^{-13} cm² and 1×10^{-14} cm² are also plotted using eq. (2). The lines drawn through the experimental points are meant only as a guide. The decay rates are indicative of a Coulombically attractive trap.

we have calculated the capture cross-section for annihilating the E' center by electrons. The thermal oxides were flooded with holes as described above (resulting in the generation of E' centers and positive charge), and subsequently flooded with a known number of electrons. To estimate the number of electrons injected, a positive voltage on the oxide surface was applied using corona ions. This voltage was measured using a Kelvin probe and an electrostatic voltmeter. By measuring the decay in the corona ion bias during UV illumination, the number of electrons photoinjected into the oxide can be calculated from $C_{ox}V = Q$. Figure 4 presents our results. Assuming that the positively charged E' centers are annihilated by electron capture, and assign a capture cross-section, σ, to this center, the E' annihilation may be described by first order trapping kinetics [48,49],

$$dE'/dt = -\sigma E'(dn_e/dt),\qquad(1)$$

where E' is the volume density of E' centers and n_e is the number of electrons injected into the oxide per cm². Integrating, we obtain

$$E' = E'_{VUV}\exp(-\sigma n_e),\qquad(2)$$

where E'_{VUV} is the maximum E' concentration following VUV illumination (hole flooding).

Fig. 3. Schematic illustration of the hole trapping process followed by subsequent electron capture in the oxygen vacancy model.

Figure 4 plots the normalized E' and positive charge density versus the concentration of electrons injected into the oxide, n_e. Again the numbers of positive charge and of E' centers exhibit similar trends. Figure 4 also plots the expected decay in the E' density assuming that the capture cross-section is either $\sigma = 1 \times 10^{-13}$ cm^2 or 1×10^{-14} cm^2 using eq. (2). Even though a single capture cross-section could not be fit to our data, the range of capture cross-sections is close to that for a Coulombically attractive (positively charged) trap [49].

At this time, we would like to further argue that the E' centers in our experiments are generated by hole capturing events at pre-existing oxygen vacancies. Our results cannot be interpreted by an oxygen displacement or by some sort of precursor transformation that may occur during a non-radiative decay of excitons (from a laser [50,51]). Because an electric field was applied during the illuminations, the photo-generated electron/hole pairs are separated, inhibiting exciton formation, and the subsequent generation of permanent oxygen vacancies that may occur due to their non-radiative decay [51].

Even though the cycling experiments are consistent with the FFY oxygen vacancy model, and the E' center is a deep hole trap in these MOS thermal oxides, it cannot generally be concluded that E' centers are always responsible for the positive charge in a thermal oxide. There are examples in which this is not the case, i.e., thermal oxides subjected to high electric fields [52–54] or the negative bias temperature instability [55]. Likewise, recent hole flooding work by Yokogawa et al. [56] shows that the E' center is not the nature of the hole trap in their thermal oxides.

4. Experimental details – sol–gel silicates

The high surface area silicate gels (surface area 850 m^2/g) were prepared using a two-step acid–base hydrolysis procedure described in ref. [57]. After gelation at room temperature, the solvent (ethanol) was evaporated at 60°C. The gels were then heated at 1°C/min to 400°C in air and held at 400°C for 2 h to oxidize organics. The

samples were then annealed at 1°C/min to 650°C, held at this temperature for 60 h in vacuum (10^{-7} Torr), cooled to room temperature, and sealed in glass test tubes under vacuum. Previous ^{29}Si MAS-NMR and Raman spectroscopic studies indicated that after heating to 650°C the gels contained over 2.2 cyclic trisiloxanes/nm^2 of surface [45] and exhibited a very intense 608 cm^{-1} Raman active vibration, labeled D$_2$ [58].

During gamma irradiations (^{60}Co) and ESR measurements, the gels were maintained under dry conditions. A second set of experiments was performed on the gels after exposure to 100% relative humidity at room temperature for either 1, 3, 12 or 24 h. The ESR measurements were made at room temperature for the E' centers and 120 K or room temperature for the OHCs. The spectra for the E' centers (OHCs) were taken using a microwave power of 5 μW (5 mW) and a modulation amplitude of 0.2 G (2.5 G). Because of the interference of the E' center with the OHC, we used the amplitude of the positive maximum-negative minimum of the OHC spectrum as an indication of the relative numbers of the defect. By comparing the spectra to a calibrated spin standard (strong pitch) spin concentrations were determined using a TE$_{104}$ cavity. The absolute spin concentrations are accurate to about a factor of two.

Before presenting our ESR and Raman scattering results on the silicate gels, we discuss evidence regarding the structural origin of the Raman active 608 cm^{-1} D$_2$ band. Our conclusions regarding the precursor of the E' center in some silicate gels are based upon Galeener's 'generally' accepted model [33–39] (see ref. [59] for a differing interpretation) of the D$_2$ band, namely, oxygen ring-breathing vibrations of a highly regular, planar, strained, cyclotrisiloxanes.

5. D$_2$ band in silicates

Prominent features in the Raman spectra of silicate gels are illustrated in fig. 5. The spectra consist of narrow bands at 490 and 608 cm^{-1} and broad features at 430, 800, 1065 and 1200 cm^{-1}. The broad features can be understood in terms of

the vibrations of a continuous random network model [60,61]. The narrow bands at 490 and 608 cm^{-1} could not be explained by that model.

The evidence relating the structural origin of the D_2 band found in conventional fused silica and high surface area silica gels to cyclic trisiloxanes (three-membered rings) is by now quite compelling. For instance, Brinker et al. [33] have performed ^{29}Si nuclear magnetic resonance and Raman scattering studies of high surface area silica gels demonstrating that the 608 cm^{-1} D_2 band is related to reduced Si–O–Si bond angles. The correlation [62] of the ^{29}Si chemical shift and the Si–O–Si bond angle, ϕ, indicated that the structures responsible for D_2 have $\phi = 137°$ consistent with the formation of three-membered rings according to reaction (3):
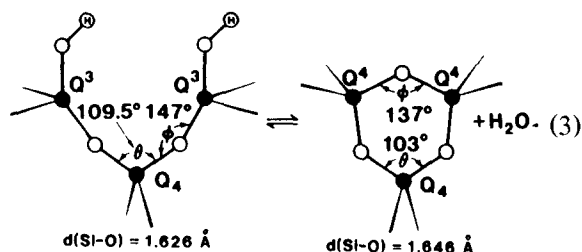
Hydrolysis of the rings according to the reverse of reaction (3) was shown to increase the average Si–O–Si bond angle to 147° (eliminate strain) and severly reduce the D_2 band to a level comparable to well annealed conventional a-SiO₂ [33].

6. Sol–gel silicate results

Exposure of the silicate gels to water vapor for increasing times at room temperature results in a monotonic decrease of the Raman D_2 band, as illustrated in fig. 5. This hydrolysis result has been explained by Brinker and co-workers [33,37] and is consistent with the work of Michalske and Bunker [63] dealing with strain enhanced reactivity of Si–O bonds.

Figure 6 shows the ESR spectra of E' centers in gamma irradiated (220 MRad) silicate gels with differing D_2 concentrations. Figure 6 (a)–(c) correspond to the samples shown in fig. 5 (a)–(c), respectively. For example, the sample used in fig.
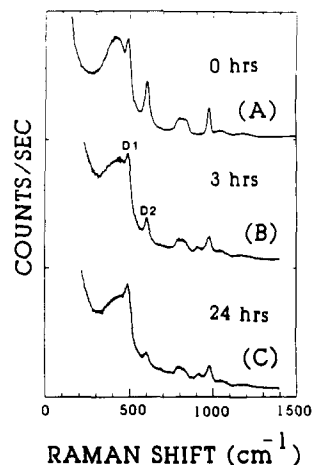

Fig. 5. Raman spectra of sol-gel silicates exposed to water vapor for various times: (a) 0 h, (b) 3 h and (c) 24 h.

6(a) has the largest D_2 concentration; the sample used in fig. 6(c) has the smallest D_2 concentration. As fig. 6 demonstrates, the irradiated silicate gels with the largest D_2 concentration have the largest concentration of E' centers (this is especially evident at high irradiation doses); the gels with the smallest D_2 concentration have the smallest concentration of E' centers.

Figure 7 illustrates the relative E' concentration as a function of irradiation dose for silicate
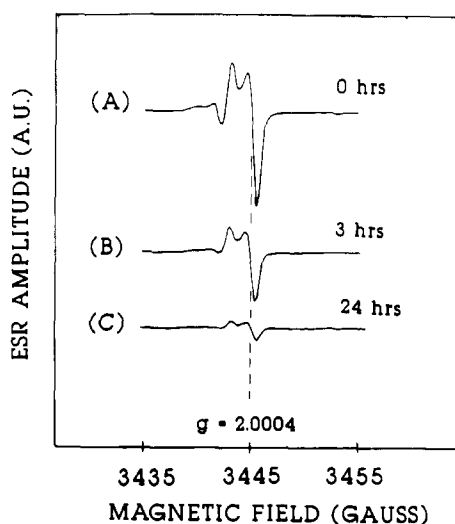

Fig. 6. ESR spectra of E' centers in irradiated silicate gels exposed to water vapor for various times: (a) 0 h, (b) 3 h and (c) 24 h. All samples were subjected to 220 MRad.
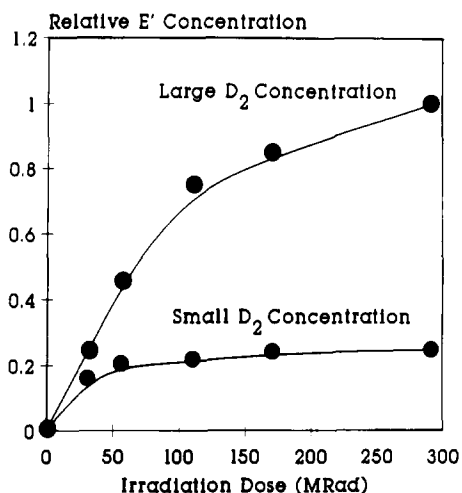
Relative E' Concentration

Fig. 7. Relative E' concentration as a function of irradiation dose for silicate gels with different D_2 concentrations. The lines drawn are meant only as a guide to the eye.
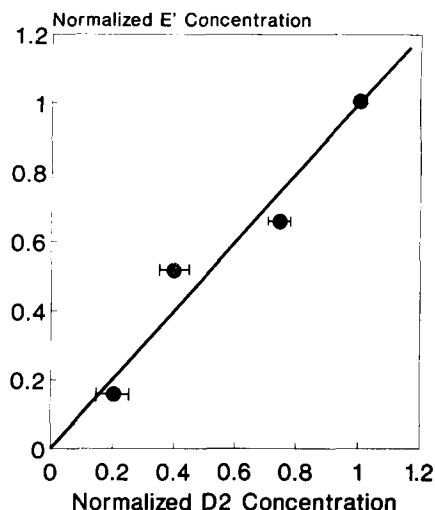
Normalized E' Concentration

Fig. 8. Plot of the relative D_2 intensity vs. the relative E' concentration for silica gels exposed to water vapor for 0 h, 1 h, 3 h and 24 h and subsequently irradiated to 220 MRad. The D_2 intensity was calculated using the psuedo-first order rate constant of $5.2 + 10^{-3}$/min given in ref. [64]. The relative error in E' is 10%. The line drawn simply represents the situation assuming a 1:1 correlation between D_2 and E'.

gels with differing D_2 concentrations. (The sample with the larger D_2 intensity was not exposed to water vapor; the silica gel with the smaller D_2 intensity was exposed to water vapor for 12 h.) The concentration of E' centers in the sample with the largest D_2 concentration after 290 MRad is 7×10^{15}/g.

In fig. 8, we plot the normalized D_2 concentration vs. the normalized E' concentration. The D_2 peak in the gel not exposed to H_2O vapor was normalized to one. The four samples correspond to silicate gels exposed to water vapor for 0 h, 1 h, 3 h and 24 h. We calculate the normalized D_2 intensity using the psuedo first order rate equation for the hydrolysis of three-membered rings exposed to water vapor [64], i.e., the rate constant is $5.2\ (\pm 0.5) \times 10^{-3}$/min. As can be seen, there appears to be correlation between the D_2 species and the number of radiation induced E' centers.

Figure 9 illustrates the relative concentration of OHCs [65] vs. irradiation dose for the samples for which data is shown fig. 7. As shown, the concentration of OHCs is also greater in the silicate gels with the largest D_2 concentration. The concentration of OHCs is approximately 7×10^{15}/g. The concentrations of E' centers and OHCs are not very large in comparison to bulk vitreous a-SiO₂; this may result because the gels

are prepared at very low temperatures and have extremely high surface areas compared to bulk a-SiO₂. In these different forms of silica, different paramagnetic precursors are likely to predominant.
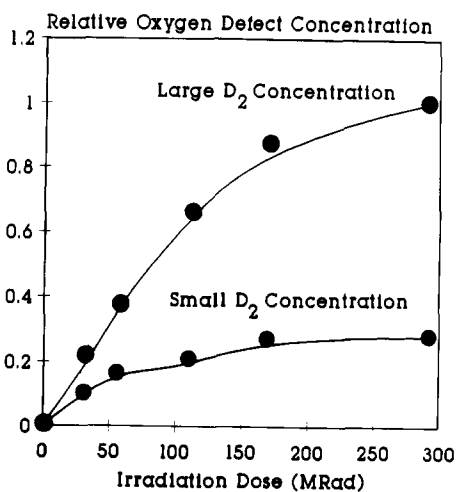
Relative Oxygen Defect Concentration

Fig. 9. Relative oxygen hole center concentration vs. irradiation dose of silicate gels with different D_2 concentrations. The samples used were the same as those used in fig. 7. The lines drawn are provided simply as a guide to the eye.

Figures 6–9 show that the concentration of radiation induced point defects is greater when the relative concentration of Raman D_2 species is greatest. Assuming that bond strain due to the small rings increases radiation sensitivity, this observation may provide evidence for a new fundamental precursor to both the E' center and OHCs [65] involving strained Si–O bonds.

7. Discussion

7.1. Alternative models

At this point, we discuss some alternative explanations of our data. For instance, it could be argued that the water vapor exposures not only decrease the concentration of three-membered rings, but also the concentration of oxygen vacancies which are known to be precursors to the E' center. In this case, the correlation between the D_2 concentrations and the gamma irradiated E' and OHC concentrations would be casual, not causal, i.e., upon exposure to water vapor, the D_2 band and E' and OHC precursors may be removed by separate parallel reactions albeit with virtually identical rates. We discuss the consequences/significance of this in the following paragraphs.

First, since these gels were originally synthesized from well defined $Si(OC_2H_5)_4$ molecules in an aqueous environment and have never been heated above 650°C, it is unlikely that measurable quantities of oxygen vacancies are present in dehydroxylated gels, and therefore that exposure to water vapor will produce a measurable reduction of them. For example, Galeener [66] has shown that for conventional a-SiO₂ the number of E' precursors (presumably oxygen vacancies) decreases with glass fictive temperature as does the D_2 band. Thus, for glasses never heated above 650°C, the number of pre-existing oxygen vacancies should be very small. Therefore, oxygen vacancies and their possible destruction/creation by water vapor/dehydroxylation should not greatly contribute to our results. By contrast, the concentration of strained bonds in the dehydroxylated gels is much larger than that in a-SiO₂ due

to the high concentrations of three-membered rings. The predominant effect of water vapor in this case is simply the hydrolysis of strained Si–O bonds according to the reverse of reaction (3).

Second, further evidence of a causal relationship between strained three-membered rings and gamma irradiated E' generation is that both the strained siloxane bonds and the E' (and OHC) precursors are located in close proximity to the surface and exhibit virtually identical responses to water vapor exposure. The diffusion constant of water in a-SiO₂ is $< 5 \times 10^{-20}$ cm²/s at room temperature [67]; therefore, water can diffuse only about 6 Å in 24 h at room temperature, requiring both the strained siloxane bonds and the E' (and OHC) precursors to be located within this surface affected region. Further, fig. 7 shows approximately a 1:1 dependence of the change in E' concentration with change in strained cyclotrisiloxanes (D_2) upon exposure to water vapor. We suggest that for the strained siloxane bonds and the E' precursor to be located near the silica surface and to exhibit practically identical responses to water vapor exposure indicates that the strained siloxane bonds and E' precursors are one and the same.

Third, in several instances [68,69] SiOH, rather than oxygen vacancies, have been suggested as precursors to the E' center. Devine [68] suggested that SiOH precursors might explain the significant increase in the E' defect creation in gamma irradiated undensified and densified wet silica (Suprasil 1) as compared with dry silica (Suprasil W1). Our results clearly show the opposite trend, namely, exposure of comparatively dry gels to water vapor creates SiOH groups according to the reverse of reaction (3), yet after gamma irradiation fewer E' centers were generated. We do not mean to overemphasize this suggested precursor model to the E' center, since it may pertain in only limited cases; nonetheless, it supports the idea that exposing the gels to water vapor does nessecarily destroy supposed E' precursors.

Fourth, Stapelbroek, Griscom and co-workers have shown that SiOH is the most likely the precursor to the NBOHC [7,24,25]. Therefore, exposure of the gels to water vapor, which causes

the formation of SiOH according to the reverse of reaction (3), might be expected to increase the OHC concentration after irradiation. Our results show an opposite trend: exposure to water vapor causes a reduction in the OHC concentration after gamma irradiation as illustrated in fig. 9. Thus, SiOH must not be the predominant OHC precursor in this case. The close correspondence of the OHC and E' concentration with dose suggests that the E' and OHCs are created by the same mechanism.

Although the arguments put forth are not unambiguous proofs in and of themselves, they suggest that the dominant E' and OHC precursors in the dehydroxylated gels are strained siloxane bonds contained in three-membered rings and that the E' and OHC form by the rupture of strained silicon–oxygen bonds.

Since we do not observe any broadening or distortion of the E' spectrum due to dipole–dipole interactions (which one would expect for two unpaired spins in close proximity), the E' centers and OHC, once generated, must separate to a distance of at least 15 Å. Therefore, it is unlikely that an E' center and OHC are nearest neighbors as expected for the simple reaction,

$$h\nu + O_3{\equiv}Si-O-Si{\equiv}O_3{-}{-}{-}O_3{\equiv}Si \cdot + \cdot O-Si{\equiv}O_3.$$

(4)
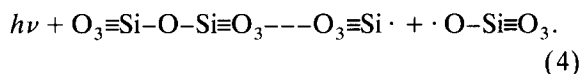
The process is undoubtedly more complicated. They may be created as such but other processes cause their ultimate separation.

7.2. ^{29}Si hyperfine interactions

In fig. 10 we illustrate the ^{29}Si E' hyperfine structure of irradiated (a) Suprasil 1 and (b) silicate gels that have a large D$_2$ concentration. The ^{29}Si E' hyperfine structure of Suprasil 1 is shown for comparison only. (The ^{29}Si E' hyperfine spectra of Suprasil 1 has been reported previously by Griscom et al. [10].)

Hyperfine interactions result from the interaction of an unpaired electron with a nucleus with a magnetic moment. Since ^{29}Si has a spin $I = 1/2$, a two-line ESR spectrum results as shown in fig. 10. The hyperfine lines in fig. 10(a) and (b) were
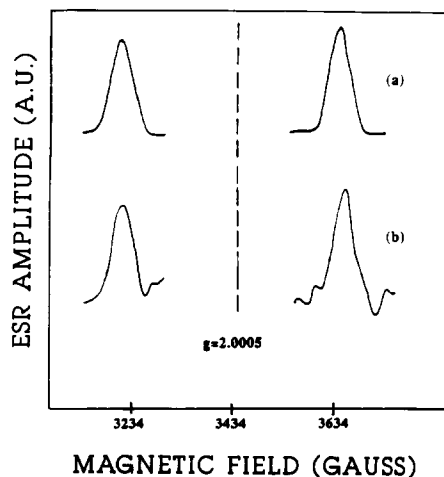

Fig. 10. ^{29}Si E' hyperfine spectra of (a) Suprasil 1 and (b) a high surface area sol–gel silicate with a large D$_2$ concentration.

observed in an out of phase second harmonic detection mode at relatively high microwave power (30 mW). Under these conditions, it has been found that the detected signal represents the absorption of the spectrum (approximately) rather than the second derivative of the spectrum [26]. (^{29}Si is only 4.7% abundant.) This detection scheme has been used by a number of authors with success [26,70,71].

From an observation of fig. 10(a) and (b), it is quite obvious that the ^{29}Si hyperfine spectra are identical, within errors of measurements, for the gamma irradiated sol–gel silicate with a large concentration of D$_2$ species and the Suprasil 1. (As expected, the ^{29}Si hyperfine spectra of our Suprasil 1 sample is identical to that reported by Griscom et al. [10].) From a computer analysis of the ^{29}Si hyperfine spectra, Griscom et al. [10] were able to show that the unpaired electron is highly localized on an sp^3 hybridized orbital on a silicon bonded to three oxygens. The E' center in the silicate gel with a large concentration of strained silicon–oxygen bonds can be described in this way.

It should be stressed that the Raman spectra of Suprasil 1 (extensively illustrated in the literature [72,73]) exhibit a significantly smaller Raman D$_2$ band intensity compared with the high surface area silica gels; therefore, it seems unlikely that

strained Si–O bonds, at least in a three-membered ring, are the predominant E′ precursors in Suprasil 1. (As discussed above, strained Si–O bonds also exist in regular forms of silica; thus, it could be argued that the strained sites in regular silica also serve as precursors to radiation induced defects as we have argued for the three-membered rings.) Nonetheless, the ^{29}Si E′ hyperfine spectra are essentially identical for the Suprasil 1 and the sol–gel silicates with large D_2 concentrations. The rupture of a strained bond may release most of the strain, allowing the E′ center to relax back to its 'equilibrium' configuration. This observation may indicate that the strain of the three-membered ring is somewhat localized, once the ring is ruptured the strain is released. (The hydrolysis of the strained Si–O–Si bond also causes the total reduction of stress [33].) It is quite interesting that the work of Devine and Arndt [70] found that the ^{29}Si hyperfine spectrum is dependent on silica densification. It is possible that their densified silica is under a greater strain and is not local in nature since the E′ center does not relax back to equilibrium. These observations may also be explained by assuming that the surface can relax more easily than the bulk. These results demonstrate that the ^{29}Si E′ hyperfine spectra do not necessarily lead to an unambiguous identification of E′ precursor structure. It can, however, provide information regarding E′ defect structure, as shown in other studies [9,10].

8. Conclusions

We have provided experimental evidence for two fundamentally different E′ precursors in amorphous silicon dioxide – namely, oxygen vacancies and strained cyclotrisiloxanes (three-membered rings). In thermally grown silicon dioxide films, we have been able to provide further evidence that E′ precursors are oxygen vacancies, and that the oxygen vacancy E′ center is positively charged when ESR active.

In another silicate system, i.e., high surface area silica gels, we find that the concentrations of both E′ centers and OHCs increase with the concentration of strained three-membered rings,

and that the E′ and OHC generation exhibit quite similar dose dependences. The normalized E′ concentration is proportional to the normalized concentration of three-membered rings and both the E′ and the strained siloxane bonds are located in close proximity to the silica surface. Collectively this evidence is consistent with the hypothesis that strained siloxane bonds are precursors to both E′ centers and OHCs. With the various kinds of E′ centers, as also discussed by Griscom [26], it becomes quite apparent that defect analysis in amorphous silicon dioxide is complicated.

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