RELATIONSHIP BETWEEN STRAINED SILICON-OXYGEN BONDS AND RADIATION INDUCED PARAMAGNETIC POINT DEFECTS IN SILICON DIOXIDE

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We have investigated the radiation induced generation of paramagnetic point defects 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 (3-membered rings). Our results suggest a correlation between the concentration of the 3-membered rings with the concentration of radiation induced paramagnetic E' (trivalent silicon center) and oxygen centers, thus, providing the first substantive evidence of the relationship between a specific strained siloxane structure and radiation damage in amorphous silicon dioxide.

It has long been recognized that amorphous silicon dioxide ($a-SiO_2$) can be damaged by ionizing radiation [1-3], for example, it damages the insulating layers of metal oxide semiconductor field effect transistors [1]. Thus, a detailed understanding of the mechanisms and structural origins of the radiation damage process in $a-SiO_2$ is of considerable interest.

Extensive ESR studies have been performed on crystalline quartz and bulk $a-SiO_2$ subjected to various forms of irradiation [2-6]. These investigations have identified several intrinsic point defects: E' centers, peroxy radicals and non-bridging oxygen hole centers (NBOHC's). The E' center is an unpaired electron on a silicon bonded to three oxygens [4,5]. One theoretical model [7-9], also established experimentally [10], identifies the precursor of the E' center as an oxygen vacancy ($O_3Si-SiO_3$). The peroxy radical ($\cdot O-O-SiO_3$) and NBOHC ($\cdot O-SiO_3$) have been identified as two intrinsic paramagnetic oxygen centers that predominate in irradiated "dry" (< 1 ppm OH) and "wet" silicas respectively [2,3,6]. The precursors for the peroxy radical and NBOHC are believed to be an oxygen surplus site ($O_3Si-O-O-SiO_3$) [6] and a hydroxyl site

(O_3SiO-H) [2] respectively.

It has also been suggested that atomic level stress plays a role in the radiation induced damage process of $a-SiO_2$ [11-13]. Devine and Arndt [12,13] have recently provided strong evidence that this is the case by observing large defect enhancements on plastically densified fused silicas over undensified silicates. But, to date, there has not been a concrete relationship established between the aforementioned point defects and a specific strained silicate structure. In this study we provide evidence that suggests that strained cyclic trisiloxanes (3-membered rings, an n-membered ring has n-silicon tetrahedra connected by bridging oxygens) are also precursor structures to E' centers and oxygen hole centers (OHC's) [14]. We have used Raman scattering combined with previous ^{29}Si nuclear magnetic resonance (NMR) studies [15] to identify these strained silicate structures.

Prominent features in the Raman spectra of silicate gels are illustrated in Fig. 1. It is generally believed [15-20] that the sharp Raman, 608 cm^{-1}, D_2 band results from oxygen ring breathing vibrations of highly regular, planar, strained, cyclotrisiloxanes
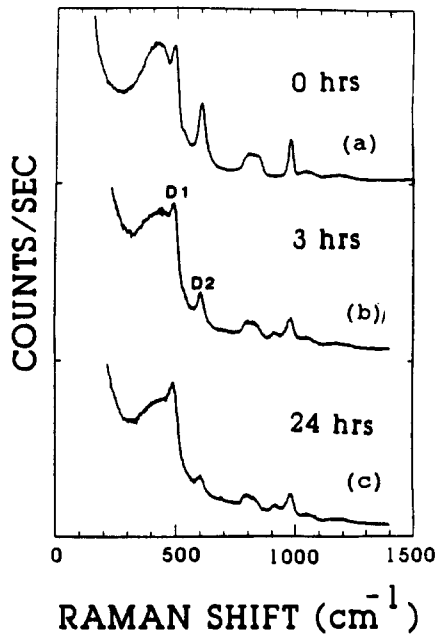
Figure 1 Raman spectra of sol-gel silicates exposed to water vapor for the various times (a) 0 hrs, (b) 3 hrs, and (c) 24 hrs.

(3-membered rings) with Si-O-Si angles $\phi = 137°$. Molecular orbital calculations [20] of 3-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 1.646Å). The average structure of a-SiO$_2$ is believed to consist mainly of puckered, unstrained, 5-8 membered rings with an average $\phi = 149°$ [21]. Diffraction studies [22] clearly indicate that regular forms of SiO$_2$ contain a wide range of Si-O-Si intertetrahedral bond angles. Bond angle (energy) calculations [23] indicate that strained bonds also exist in regular forms of silica due to bond angle variations from 149°; these sites may also be precursor sites to radiation induced defects.

To establish a relationship between radiation induced point defects and strained silicate structures we have irradiated high surface area sol-gel silicates with varying relative intensities of the Raman D$_2$ band. 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 D$_2$ Raman band is present in virtually all

forms of a-SiO$_2$, i.e., fused silica [16], thermally grown SiO$_2$ films on Si [24]. 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$_2$ [18]; the only difference is that the concentrations of these rings in the dehydroxylated gels are significantly larger.

The evidence regarding the structural origin of the D$_2$ band found in conventional fused silica and high surface area silica gels is quite compelling. (1) The relative intensity of D$_2$ increases with glass fictive temperature [19] with an activation energy that agrees with molecular orbital calculations for the heat of formation of 3-membered structures [20] and with that found by differential scanning calorimetry measurements [18] in sol-gel glasses.

(2) Galeener et al. [17] calculated the force constants needed to vibrationally decouple these "defect" bands from the continuous random network, thereby, explaining the narrow lines as well as the lack of silicon motion. (3) Brinker et al. [15] have performed ^{29}Si NMR 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 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 strained 3-membered rings [15,18] according to:

$$O_3Si-OH + HO-SiO_3 - O_3Si-O-SiO_3 + H_2O \quad (1)$$
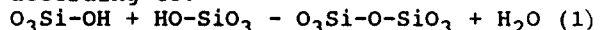
We use high surface area silica gels prepared in an identical manner as in the NMR studies to establish the relationship between siloxane bond strain and radiolysis in this study. The high surface area silica gels (surface area 850 m^2/g) were prepared using a two-step acid-base hydrolysis procedure described in Ref. 18. After drying at 60°C the gels were heated at 1°C/min to 400°C in air, and held at 400°C for 2 hrs to oxidize the organics. The samples were then annealed at 1°C/min to 650°C, held at that temperature for 60 hrs in vacuum (10^{-7} Torr), cooled to room temperature, and sealed in glass test tubes under vacuum. During the gamma irradiations (^{60}Co), ESR, and Raman scattering measurements the gels were maintained under rigorously dry conditions. Another set of experiments were performed on gels exposed to 100% relative humidity at room temperature for either 3, 12 or 24 hrs; after exposure to water vapor the gels were gamma irradiated.

The ESR measurements were made at room temperature for the E' centers and at either room temperature or 120K for

the OHC's. The spectra for the E' centers (OHC's) were taken using a microwave power of 5 μW (5 mW). 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 behavior of the defect density. By comparing the spectra to a calibrated spin standard (strong pitch) spin concentrations were determined.

Exposure of the silicate gels to water vapor for increasing times results in a monotonic decrease of the Raman D_2 band as illustrated in Fig. 1. The Raman data was not normalized in this figure and the Rayleigh wing was not subtracted. The extent of hydrolysis on the D_2 band was previously examined by normalizing to the 430 cm^{-1} band [25]. This hydrolysis result has been explained by Brinker et al. [18] and is consistent with the work of Michalske and Bunker [26] dealing with strain enhanced reactivity of Si-O bonds. We believe that the water vapor is simply hydroxylating strained Si-O bonds thereby releasing the strain according to the reverse of reaction 1. Since these gels were originally synthesized in an aqueous environment, and have never been heated above 650°C, it is unlikely that measurable quantities of oxygen vacancies are present in the dehydroxylated gels, and that exposure to water vapor will produce a measurable reduction in oxygen vacancies. For example, Galeener [24] has shown that for conventional a-SiO_2 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. 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. In contrast, this would be extremely difficult in other forms of a-SiO_2 in which the concentrations of these rings are so smaller, so other precursors of radiation damage centers may dominant.

In Fig. 2 we illustrate ESR spectra of E' centers in gamma irradiated (220 MRad) silicate gels with different B_2 concentrations. Fig. 2 (a, b, and c) corresponds to the samples shown in Fig. 1 (a, b, and c) respectively. For example, the sample used in Fig. 2(a) has the largest D_2 concentration; the sample used in Fig. 2(c) has the smallest D_2 concentration. As demonstrated, the irradiated gels with the largest D_2 concentration exhibit the largest concentration of E' centers,
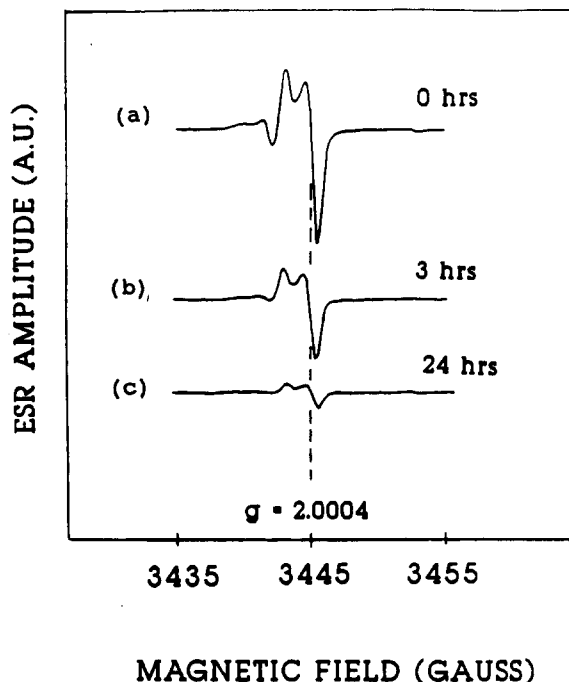

MAGNETIC FIELD (GAUSS)

Figure 2 ESR spectra of E' centers in irradiated silicate gels exposed to water vapor for the various times (a) 0 hrs, (b) 3 hrs, and (c) 24 hrs. All samples were irradiated to 220 MRad; all spectrometer settings and sample masses where identical.

8 X 10^{15} E' centers/gram.

Figure 3 illustrates the relative E' concentration as a function of irradiation dose for silicate gels with two different 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 hrs.) Note that the relative E' concentration is greater (especially at higher doses) in the silicate gel with the largest D_2 concentration.

In Fig. 4 we illustrate the relative concentration of the OHC's vs. irradiation dose for the same samples illustrated in Fig. 3. As shown, the concentration of OHC's is also significantly greater in the silicate gels with the largest D_2 concentrations. By comparing Figs. 3 and 4 one can see that the rate of generation of E' centers and OHC's is nearly identical, as also found by Devine and Arndt [12] in irradiated plastically densified Suprasil W1. The maximum concentration of OHC's in Fig. 4 is 7 X10^{15}/gram; however, it is difficult to extract a precise value (even at 120K) due to the interference of the E' center as mentioned earlier. The concentrations of the E' centers and OHC's are not very large in comparison to regular fused
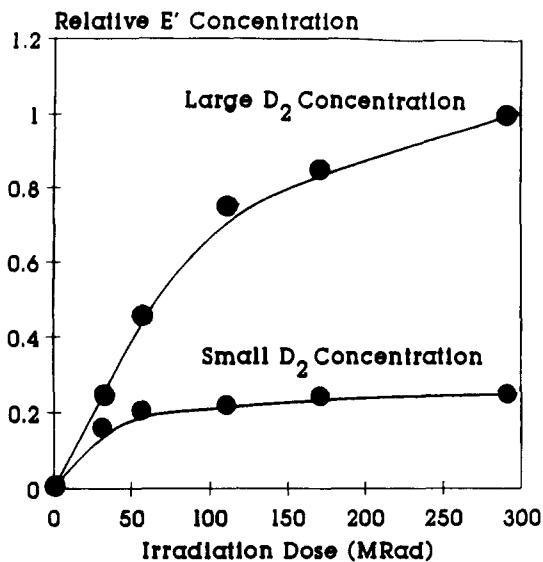
Relative E′ Concentration

Figure 3 Relative E′ concentration vs. irradiation dose for silicate gels with different D_2 concentrations.
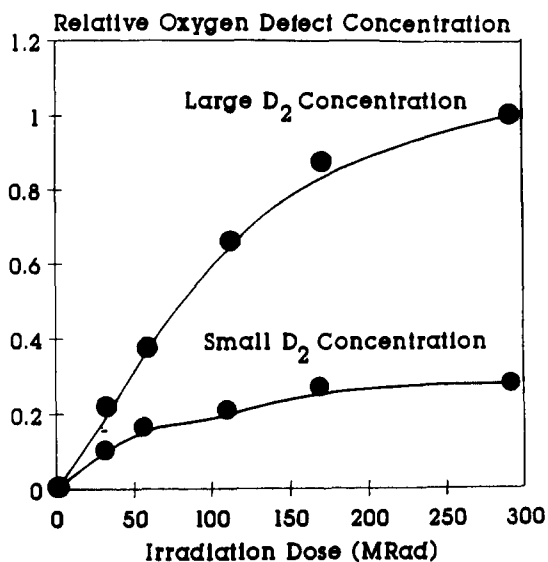
Relative Oxygen Defect Concentration

Figure 4 Relative paramagnetic oxygen center concentration vs. irradiation dose for silicate gels with different D_2 concentrations. The samples used are the same as those used in Figure 3.

silica; we believe that this is because (1) the 3-membered rings are not under a lot of strain, and the strain is local in nature, (2) the very low temperature of the gels [24] and (3) the effects we

are observing are primarily surface related. Nonetheless, the rings are strained enough that there are marked differences in the response of the gels with different concentrations of them.

Our results cannot be explained by the notion that we are destroying precursors to the NBOHC in the gels exposed to water vapor. SiOH groups are the most generally accepted precursor to the NBOHC; thus, exposure of the gels to water vapor, which causes the formation of SiOH according to the reverse of reaction (1), might be expected to increase the OHC density after irradiation. Our results show an opposite trend: exposure to water vapor causes a reduction in the OHC density after irradiation. Thus, SiOH must not predominate OHC precursors in this case. The close correspondence of the OHC and E′ densities with dose suggest a different mechanism in which E′ and OHC's are created by the same mechanism.

Figures 1 through 4 show that the concentration of radiation induced point defects is greater when the relative concentration of the D_2 species is the greatest. Assuming that bond strain due to the small rings increases radiation sensitivity, we believe that this observation suggests evidence for a new fundamental precursor to both E′ and paramagnetic oxygen centers involving strained Si-O bonds.

Since we do not observe any broadening or distortion of the E′ spectrum due to dipole-dipole interactions the E′ centers and OHC's must be at least 15Å apart. Therefore, it is <u>unlikely</u> that an E′ center and a OHC are nearest neighbors as expected for the simple reaction.

$$h\nu + O_3Si\text{-}O\text{-}SiO_3 \longrightarrow \cdot SiO_3 + \cdot O\text{-}SiO_3$$
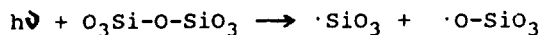
The process mechanism is undoubtedly more complicated.

In summary, we have been able to provide evidence that suggests that strained three membered rings can be precursors to E′ centers and OHC's. This observation may be of considerable importance since it provides for the first time some evidence for a relationship between a specific strained silicate structure and radiation induced paramagnetic point defects in a-SiO_2.

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