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Evidence for pair generation of an E' center and a nonbridging oxygen-hole center in γ-ray-irradiated fluorine-doped low-OH synthetic silica glasses

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We have examined effects of fluorine concentration on defect formation by γ-ray irradiation in low-OH synthetic silica glasses over the F concentration range 0–3 wt.%. Doping with 1 wt.% of fluorine eliminates effectively ≡Si−Cl without causing formation of ≡Si−Si≡ and ≡Si−H (all such structural units may be precursors of the E' center); and ≡Si−F does not behave as the precursors of the E' center. At this doping level, the concentration of the E' center is minimized, and the concentration coincides with that of the nonbridging oxygen-hole center (NBOHC). We conclude that pair generation of the E' center and NBOHC from intrinsic ≡Si−O−Si≡ bonds is observed in the samples in which the precursor defects are suppressed by proper F doping.

Among the paramagnetic defects induced by high-energy irradiation of silica glass, the E' center with an unpaired electron strongly localized in a silicon sp^3 dangling bond and the nonbridging oxygen-hole center (NBOHC) with a hole in an oxygen dangling bond are considered as fundamental defects created intrinsically from Si−O−Si networks. However, it has been shown that both defects can be formed from preexisting point defects as the precursors,[1] presumably in addition to formation through an intrinsic mechanism.

The precursors in silica glass are strongly dependent on the preparation history and are often dominant sources of radiation-induced defects. In order to discuss the mechanism of intrinsic defect formation based on such variables as the concentrations of the defects produced and their dose dependence, it is necessary to separate the part of the defects produced through the intrinsic mechanism from that originating from the precursors. In this paper, we report that fluorine (F) doping does effectively remove these precursors and make intrinsic defect formation observable with γ-ray irradiation at room temperature (RT).

F-doped silica glasses were prepared by the chemical vapor deposition (CVD) soot remelting method. Fluorine was doped using a F-containing reagent during the sintering process and its concentration was controlled by varying the amount of the reagent while keeping the sintering condition unchanged. Doped fluorine atoms are incorporated into the glass network in the form of ≡Si−F, which gives a Raman peak at around 945 cm^{-1} (Ref. 2). Samples used here are listed in Table I. The concentration of OH was estimated to be less than 1 ppm by measuring the infrared absorption. The γ-ray irradiations (^{60}Co source, dose rate 1 Mrad/h) were carried out at 77 K and at room temperature. The concentrations of paramagnetic species produced were determined by taking electron paramagnetic resonance (EPR) spectra at 77 K using a Bruker ESP300 X-band spectrometer. Absolute spin concentrations of defects were obtained to an accuracy of ~20% following the method established by one of the authors.[3]

Here, we mainly discuss the concentration of the E' center and that of the NBOHC produced by irradiation at room temperature, denoted as $[E']_{RT}$ and $[NBOHC]_{RT}$, respectively. These two defects alone gave significant

TABLE I. Samples, impurities and defect yields.

Samples	F[a] (wt.%)	Cl[b] (ppm)	Defects[c] (10^{15} spins/cm^3) Cl^0	E'	H^0
S-1	0	340	450	160	0.59
S-2	0.35	120	54	33	0.84
S-3	0.65	40	N.D.	9	0.64
S-4	0.84 ± 0.004	35	N.D.	10	0.89
S-5	0.96 ± 0.005	30	N.D.	6	3.0
S-6	2.55	< 10	36	28	0.54

[a]Estimated by the refractive index.
[b]Evaluated by chemical analysis.
[c]These defect concentrations were evaluated from EPR spectra of the samples irradiated by γ rays at 77 K to a dose of 12 Mrad.

EPR signals after irradiation at room temperature. Figure 1 shows $[E']_{RT}$ and $[NBOHC]_{RT}$ with the accumulated dose of 10 Mrad as a function of the F concentration ([F]). It is noted that $[E']_{RT}$ decreased steeply with the increase of [F] and had a minimum at around [F] = 1 wt.% (sample S-5). In contrast, $[NBOHC]_{RT}$ is nearly independent of [F]. In the sample which gave the minimum of $[E']_{RT}$, $[E']_{RT}$ coincides with $[NBOHC]_{RT}$.

Oxygen-deficient centers (ODC) are sometimes dominant sources of the E' centers.[4] In our samples, neither the 7.6-eV absorption band due to ODC(I) nor the 5.0-eV absorption band due to the ODC(II) was substantially observed.[5] It has been shown that (≡SiH+HSi≡) which results from a reaction of ODCs with H_2 at temperatures higher than 500 °C are precursors of the E' centers.[6] In the H_2-treated glasses originally containing ODCs, the concentration of atomic hydrogen $[H^0]_{77\,K}$ corresponds to that of the E' center $[E']_{77\,K}$ after γ-ray irradiation at 77 K.[7] In our samples, the contribution of SiH to generation of the E' center at room temperature is negligible, since $[H^0]_{77\,K}$ is small (Table I). The small value of $[H^0]_{77\,K}$ also confirms that the concentration of ≡Si−OH, which is another source of atomic hydrogen, is small.

Atomic chlorine Cl^0 was reported as a radiation-induced defect in certain low-OH plasma-deposited silica glasses by Griscom and Friebele.[8] After irradiation (12 Mrad) at 77 K, some of our samples showed Cl^0, however, the delocalized E' center (E'_δ) and the triplet species, both of which were suggested to have their origins in specific Cl-decorated precursor sites, were not substantially observed.[9] As shown in Table I, the concentration of Cl^0 produced at 77 K ($[Cl^0]_{77\,K}$) is correlated to the concentration of Cl which was determined by chemical analysis. The steep decrease in $[E']_{RT}$ (Fig. 1) and $[E']_{77\,K}$ (Table I) with the increase of the amount of F-doping corresponds to the decrease of $[Cl^0]_{77\,K}$. Thus, the excess of the E' centers, which is defined as $[E']_{RT} - [NBOHC]_{RT}$, is attributed to Si−Cl precursors. Since Cl^0 is not observed after irradiation at room temperature, the E' centers originating from ≡Si−Cl are, presumably, stabilized through formation of Cl_2 via diffusion of Cl^0.

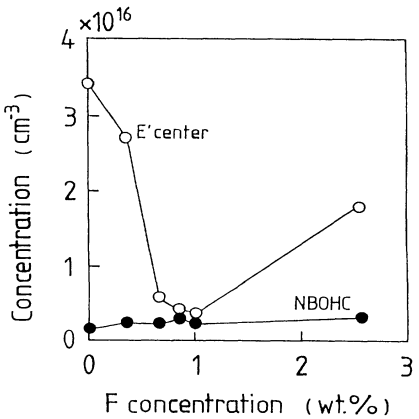

FIG. 1. Concentrations of the E' center and the NBOHC after irradiation of 10 Mrad at room temperature as a function of F concentration.

The results above indicate that ≡Si−F is not a precursor of the E' center. We did not observe EPR signals attributable to atomic fluorine F^0 after irradiation at 77 K. We showed that, in the case of irradiation of excimer lasers, the E' centers are formed through band-to-band excitation due to two-photon absorption.[10] The γ-ray irradiation creates electron-hole pairs to a concentration corresponding to the value of a few tenths of the absorbed energy divided by the band-gap energy.[11] Devine and Arndt discussed the preference of defect-formation mechanism related to electron-hole pair production rather than displacements due to collisions of Compton electrons, based on the quantitative comparison between the number of defects induced and the number of Compton electrons.[12] Molecules of SiH_4 and $SiCl_4$ show dissociative absorption bands assigned to the Rydberg transitions arising from 8.2 and 7.8 eV, respectively, while SiF_4 molecules have no absorption band below 11.4 eV.[13,14] A similar tendency in the strength of bonding is expected for Si−H, ≡Si−Cl, and ≡Si−F, which are incorporated into the glass network. It is noted that the band-gap energy of silica glass was estimated to be ~9 eV.[15] If the energy consumption occurs through the relaxation of electron-hole pairs across the band gap, the relaxation energy is large enough to break a Si−H or Si−Cl bond, but not sufficient to break the Si−F bond. Thus, Si−F may not become the precursor of E' centers.

By proper doping of fluorine (sample S-5), low-OH silica glass is attainable without introducing precursors of the E' center such as ODCs, ≡Si−H, and ≡Si−Cl. In the glasses without these precursors, $[E']_{RT}$ is still of the order of 10^{15} cm^{-3} with a dose of 10 Mrad. This part of the E' center corresponds to those formed intrinsically. In Figs. 2(a) and 2(b), $[E']_{RT}$ and $[NBOHC]_{RT}$ as a function of accumulated dose D are illustrated. In all samples studied, $[NBOHC]_{RT}$ is nearly proportional to $\sqrt{D}$. In the undoped sample (S-1), which contains a significant amount of ≡Si−Cl, $[E']_{RT}$ increases linearly with the increase of D in the range $D \lesssim 10$ Mrad. For a low-OH silica glass without precursors of the E' center (sample S-5), it is noted that

$$[E']_{RT} = [NBOHC]_{RT} \propto \sqrt{D} . \quad (1)$$

The equality $[E']_{RT} = [NBOHC]_{RT}$ suggests that in intrinsic defect formation the E' center and NBOHC are

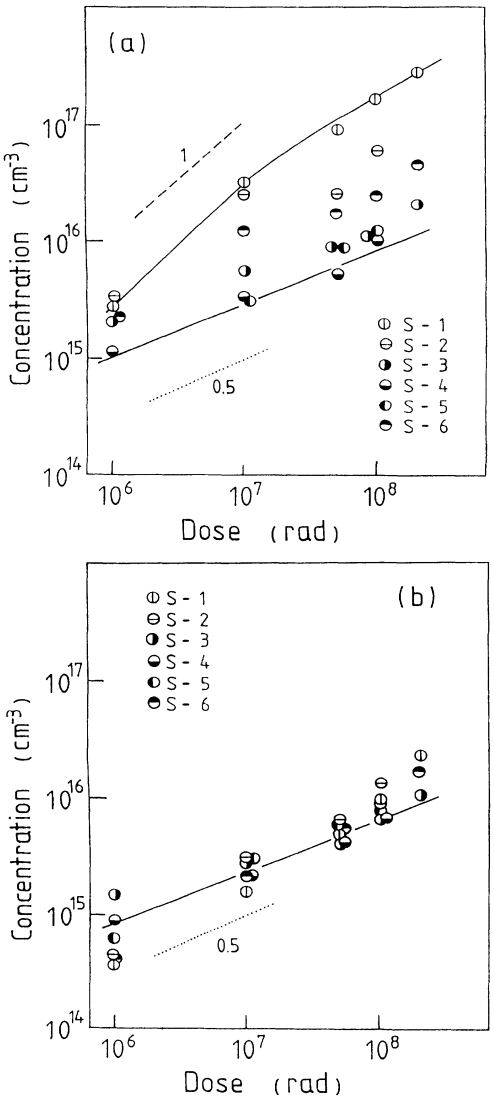

FIG. 2. Concentrations of (a) the E' center and (b) the NBOHC as a function of accumulated dose at room temperature. A dashed and a dotted line indicate the slopes 1 and $\frac{1}{2}$, respectively.

generated simultaneously in a pair, presumably from the energy dissipation of an electron-hole pair across the band gap. The generation process is schematically depicted by the following equation:

$$\equiv\text{Si}-\text{O}-\text{Si}\equiv \rightarrow \text{Si}\cdot + \cdot\text{O}-\text{Si}\equiv . \qquad (2)$$

Even though the primary process induced by γ-ray irradiation may involve Eq. (2), it is expected that other steps should follow until the stable state at room temperature is reached. Since no distinct broadening due to spin-spin interactions is noticed in the EPR signals, each E' center is separated by more than 30 Å on average from other E' centers and NBOHCs. In other words, only the defects that are separated by sufficiently large distances from other defects remain as stable species. This separation might be attained through diffusion and recombination of defects during irradiation at room temperature. If the remaining E' and NBOHC centers equilibrate with the total number of pairs of both defects temporally generated in the network through Eq. (2), a quasi-mass action law will explain the square-root dependence on the dose in Eq. (1), since $[E']_{RT}=[\text{NBOHC}]_{RT}$ holds. However, this model requires some diffusion process enhanced specially under irradiation, since no substantial suppression of $[E']$ at 77 K was observed, as shown in Table I.

One of the authors suggested another possible explanation for the equality of both defect densities, that the E' (NBOHC) center will be produced through trapping of a free electron (free hole) at precursor sites in the glass network, resulting in a negatively (positively) charged defect state.[16] Following this idea, the E' (NBOHC) will be generated by trapping of an electron (hole) following Eq. (2), where the root square dependence on D in Eq. (1) will be explained by the quenching of free carriers by the generated defects (the number of existing free carriers is proportional to the inverse of the generated defect density).

Devine and Arndt suggested a correlated creation of the E' center and NBOHC through cleavage of strained $\equiv$Si$-$O$-$Si$\equiv$ bonds based on the observation of the enhancement of the defect creation in plastically densified glasses.[12] It is expected that F doping should relax the glass network structure by increasing bond terminators $\equiv$Si$-$F. (The concentration of Si$-$Cl is much lower than that of $\equiv$Si$-$F.) However, $[\text{NBOHC}]_{RT}$ is independent of the F content (Fig. 1). As the concentration of Si$-$OH, which might be the precursor of the NBOHC is low, $[\text{NBOHC}]_{RT}$ is a useful measure of the E' centers produced intrinsically. Thus, the efficiency of the pair (the E' center and NBOHC) generation is not substantially affected by the number of bond terminators.

In contrast with the case of pair generation, the concentration of defects originating from precursors should be proportional to the dose until a saturation of the defect generation occurs with consumption of precursors. In sample S-1, $[E']_{RT}$ exhibits a typical behavior of this relation [Fig. 2(a)]. It is observed in Fig. 1 that $[E']_{RT}$ increases at high value of [F] after reaching the minimum at $[F]=\sim 1$ wt.%. We argue that the minimum value of $[E']_{RT}$ corresponds to the number of E' centers produced intrinsically and that the "excess" E' centers at low and high F contents arise from precursors. Although the Cl concentrations determined by chemical method were 120 ppm and less than 10 ppm for S-2 and S-6, respectively, $[\text{Cl}^0]_{77\,\text{K}}$ in these two samples were comparable. This shows higher efficiency of Cl^0 generation in such heavily F-doped glass.[17]

In summary, we have studied quantitatively the defect generation in F-doped low-OH silica glasses as a function of both F concentration and γ-ray dose. It was found that F doping effectively removed $\equiv$Si$-$Cl without introducing ODCs and/or $\equiv$Si$-$H and that $\equiv$Si$-$F does not behave as a precursor of the E' center. By removing the precursors of the E' center, it was revealed that the E' center formed intrinsically is generated in a pair with NBOHC. Since fluorine is one of the most important dopants to decrease the refractive index in SiO_2 fiber, proper F doping might be crucial in improving the radiation hardness.

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[17]In F-doped glasses, systematic blueshift of the absorption edge was observed with the increase of [F] until [F] reaches $\sim$1 wt.% (S-5), which implies that a latent absorption of Si—Cl at around the band edge decreases with the doping. In the case of S-6 the absorption edge shifts back to the longer wavelength, which suggests that the existing manner of Cl in the glass network of S-6 is not systematically changed as in the other samples.