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X-ray-induced absorption bands in type-III fused silicas

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X-ray-induced absorption bands in type-III fused silicas synthesized under reducing (DR) and oxidizing (DO) conditions are investigated. In sample DR, an absorption band at 5.8 eV ascribed to the E' center ($\equiv$Si$\cdot$) was induced. Photoluminescence and photoluminescence-excitation spectra suggest that the absorption band at 5.0 eV (the $B_2\alpha$ band) is caused by oxygen-deficient center ($\equiv$Si$\cdots$Si$\equiv$). In sample DO, absorption bands at 5.8, 4.8, and 2.0 eV are observed. We discuss the formation mechanism of these bands based on models proposed before.

I. INTRODUCTION

Synthetic fused silica is widely used as an optical material in the uv region because of its good optical transmission. There are several processes used to produce fused silicas;[1,2] this paper will deal with type-III fused silica. Type-III fused silica,[3] synthesized by flame hydrolysis of silicontetrachloride in a hydrogen-oxygen flame, is widely used as an optical material for the uv region, such as for excimer laser, because we can obtain a material with good optical homogeneity over a large area. However, absorption bands may sometimes be induced by radiation as in, for example γ-ray,[4,5] x-ray,[6,7] neutron,[8] and excimer lasers.[9–18]

The nature of the solarization is strongly reflected by the history of the process condition.

The authors studied,[13–18] ArF excimer laser-induced emission and absorption bands in type-III fused silicas synthesized under reducing and oxidizing conditions. When irradiated with an ArF laser, the fused silica synthesized under a reducing[15] condition shows an absorption band at 5.8 eV, ascribed to the E' center ($\equiv$Si$\cdot$),[4] and an emission band at 4.4 eV. The creation of these bands can be suppressed by annealing in ambient helium and we can obtain an ArF-laser-resistive fused silica. The fused silica was synthesized under an oxidizing condition;[16] on the other hand, an absorption band at 4.8 eV and an emission band at 1.9 eV are induced by irradiating with the ArF laser. The creation of the 4.8 and the 1.9 eV bands was strongly enhanced by annealing in ambient helium.

Nakamura *et al.*[6] reported x-ray-induced solarization of type-III fused silica. They showed, in type-III fused silica, that absorption bands at 4.8 and 5.8 eV were induced by irradiating with an x-ray beam. Although the history of the process condition of their material is not clear, the nature of the solarization seems to be different from that of the ArF-laser-induced solarization; in the fused silicas irradiated with the ArF laser, the 5.8- and the 4.8-eV bands are observed in different samples. Such a difference must result from the difference of the photon energies of the x-ray (≈ 10 keV) and the ArF laser (6.4 eV).

In this paper, we study the characteristics of x-ray-induced absorption in the fused silicas synthesized under reducing and oxidizing conditions. Moreover, we compare those results with the ArF-laser-induced luminescence and absorption bands, and discuss the creation mechanism of the solarization.

II. EXPERIMENT

Type-III fused silicas were synthesized by flame hydrolysis of silicontetrachloride in a hydrogen-oxygen flame. We used samples synthesized under two different conditions:

Sample DR: synthesized under reducing conditions, i.e., $[H_2]/[O_2] > 2.0$ in the flame and containing about 800 ppm of OH in weight.

Sample DO: synthesized under oxidizing conditions, i.e., $[H_2]/[O_2] < 2.0$ in the flame and containing about 1200 ppm of OH in weight.

The samples were cut from almost the same position of the same ingots as in the previous studies.[15,16] They were cut into a size of $10 \times 10 \times 30$ mm^3 and all surfaces were polished.

The x rays were exposed utilizing the x-ray beam of a fluorescence x-ray spectrometer (a Rigaku type 3080) with a rhodium target tube operated at 50 kV, 50 mA. The x rays were exposed to one side of the surface in a vacuum ($\approx 10^{-2}$ Torr) at room temperature. The induced absorption was measured in air at room temperature after being irradiated for a period using a spectrophotometer (a Shimadzu UV-3101). This process was repeated until the total exposure time reached 180 min.

Photoluminescence (PL) and photoluminescence-excitation (PLE) spectra were measured by using a fluorescence spectrophotometer (a Jasco FP-770). The PL and the PLE spectra were measured after irradiating with x rays for 180 min.

III. RESULTS

A. Induced absorption

Figure 1 shows x-ray-induced absorption spectra of both samples. The absorption spectra shown here are internal absorption, i.e., spectra of the difference between before and after irradiation. The fused silica synthesized under oxidizing conditions (DO) shows absorption bands at 4.8 and 5.8 eV. In addition to these bands, an absorption band at 2.0 eV was observed a shown in Fig. 2. On the other hand, in fused silica synthesized under reducing conditions, only a 5.8 eV band was induced.

Nakamura *et al.*[6] reported that the type-III fused silica irradiated with x rays shows absorption bands at 5.8 and 4.8 eV. Although they used x rays from the Cu target, the x-ray exposure effects are the same as in the present case. Therefore, their sample must be a fused silica synthesized under oxidizing conditions.

In previous papers, we studied the ArF-laser-induced absorption in both samples. In sample DO,[16] the induced absorption is not clear in the as-prepared sample, but the creation of absorption was enhanced by annealing in ambient helium at 900 °C for 2 h. Absorption bands at 4.8 and 2.0 eV appeared, but the 5.8-eV absorption bands were not observed. In sample DR,[15] on the other hand, only the 5.8 eV band was induced, as in the case of the x-ray irradiation. The creation of the 5.8-eV band can be suppressed by annealing in ambient helium.

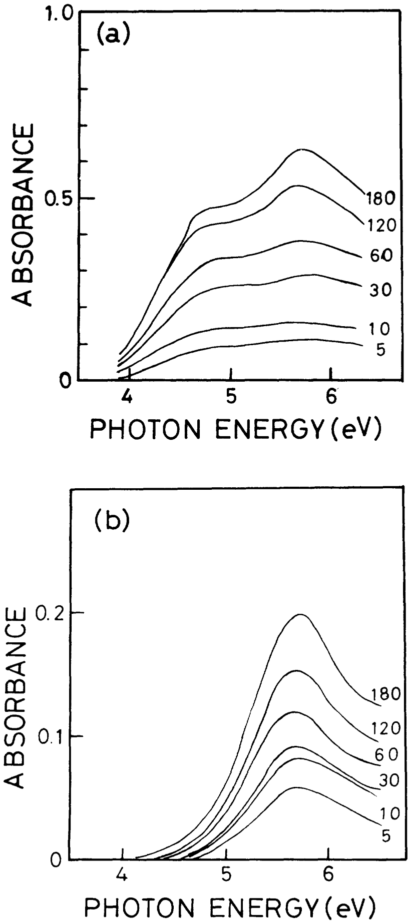


FIG. 1. X-ray-induced absorption band in samples DO (a) and DR (b). Numbers in the figure indicate the irradiation time in min.

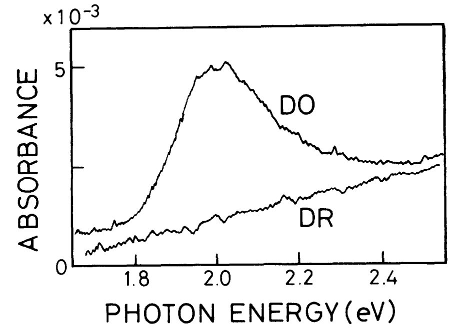


FIG. 2. Absorption band near 2 eV irradiated with x ray for 3 h.

Figure 3 shows the irradiation-time dependence of the absorption intensities at the peak positions of these bands. The absorption intensities of the absorption peaks in sample DO are proportional to the square root of the exposure time. In sample DR, there are two square-root time-dependent regions of the absorption intensity at 5.8 eV.

B. PL and PLE spectra

Figure 4 shows PL and PLE spectra of both samples. In sample DO, PL bands at 1.9, 2.8, 2.2, and 4.0 eV are observed. At 1.9 eV, a PLE band at 4.9 eV was observed. This band corresponds to the 4.8-eV absorption band induced by x-ray and ArF-laser irradiation. PLE spectra measured at 4.0 eV show peaks at 5.9 eV and >6.2 eV. The PLE spectra measured at 2.8 and 2.2 eV show a peak at >6.2 eV. Nakamura *et al.*[6] reported PL and PLE bands in type-III fused silica. They observed PL spectra at 4.3, 3.0, and 1.9 eV. The 2.2-eV band was not observed in their sample. The 1.9-eV emission band is excited only by the 4.8-eV band. The emission band at 4.0 eV is excited by the 5.9-eV PLE band, and PLE spectra at 2.8 and 2.2 eV are excited by the absorption band near 6 eV.

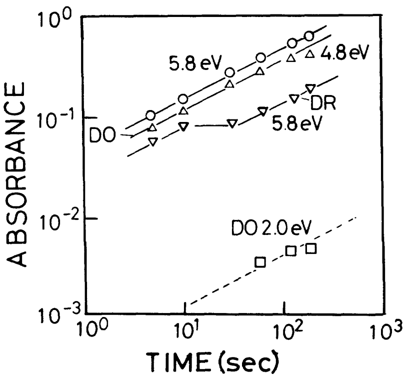


FIG. 3. Irradiation-time dependence of absorption intensities at absorption peaks.

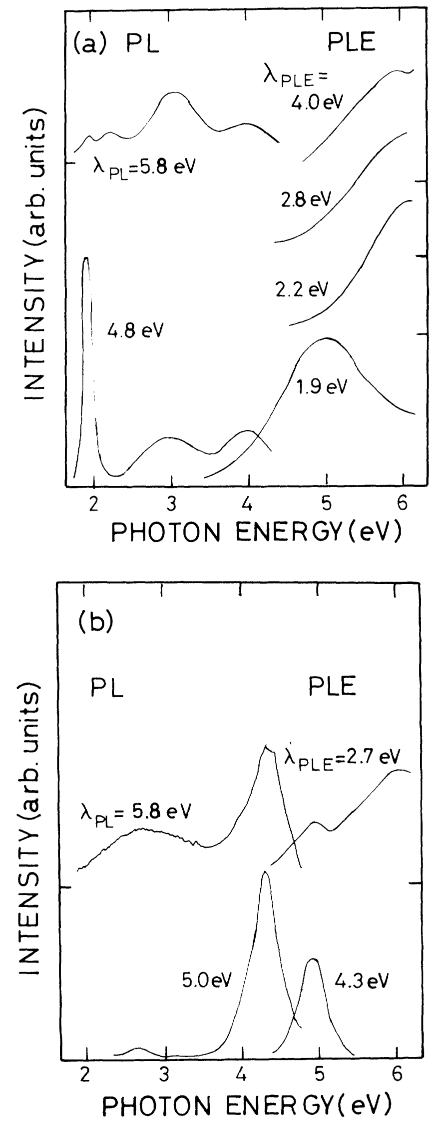


FIG. 4. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of samples DO (a) and DR (b).

In sample DR, PL bands at 2.7 and 4.3 eV were observed. A PLE band at 4.9 eV was observed by measuring the PLE spectra at 2.7 and 4.3 eV. This band is different from the 4.8-eV band in sample DO because their bandwidths are quite different from each other. In addition to the 4.9-eV PLE band, a PLE band at 5.9 eV was observed by measuring the PLE spectra at 2.7 eV; the 2.7-eV emission band is excited with the 5.9-eV band caused by the E' center.[6]

IV. DISCUSSION

A. Defect structure in sample DR

The authors discussed in previous papers the ArF-laser-induced absorption and luminescence spectra in type-III fused silicas.[15,16] We will review briefly these results: In sample DR (Ref. 15) irradiated with the ArF laser, an absorption band at 5.8 eV ascribed to be the E' center was induced. Intensity of the 5.8-eV band decays after cessation of the irradiation as shown in Fig. 5; the characteristic time of the relaxation is about 1000 sec. The precursor of this band can be annealed out with various gases. The most effective annealing gas is helium. From these results we proposed that the precursor of the 5.8-eV band is the $\equiv$Si—H H—O—Si$\equiv$ structure. Irradiated with the ArF laser, the E' center is induced by the following process:

$$\equiv\mathrm{Si{-}H\;H{-}O{-}Si}\equiv \xrightarrow{h\nu} \equiv\mathrm{Si{\cdot}H{-}O{-}Si}\equiv +\mathrm{H}\,, \tag{1}$$

and the precursor is annealed by

$$\equiv\mathrm{Si{-}H\;H{-}O{-}Si}\equiv \xrightarrow{\text{annealing}} \equiv\mathrm{Si{-}O{-}Si}\equiv +\mathrm{H_2}\,. \tag{2}$$

Now we will discuss the characteristics of the x-ray-induced 5.8 eV absorption band. Square-root dependence of the intensity of the 5.8-eV band on the irradiation time suggests that the creation process of the 5.8-eV band is concerned with a diffusion controlled reaction. Existence of the two square-root dependence region in Fig. 3 suggests that there exist two different mechanisms to produce the E' center: (i) induced easily from a precursor and saturated in a relatively short time, i.e., ≈ 10 min, and (ii) creation of the band lasted for a long period, i.e., at least a few hours. The fast part must correspond to the creation of the E' center from the $\equiv$Si—H H—O—Si$\equiv$ structure, because the characteristic time of this stage, 10 min is almost the same as the relaxation time of the H_2 recombining in the right-hand side of Eq. (2).[15] The square-root dependence corresponds to the diffusion of hydrogen in the right-hand side of Eq. (1).

The diffusion process of the hydrogen in sample DR irradiated with the ArF laser consists of three states: (i) diffusing the hydrogen atoms from the vicinity of the defect structure, (ii) forming hydrogen molecules by reacting with diffusing hydrogen atoms, and (iii) the hydrogen molecules diffusing out from the glass network. In fact, the decay of the 5.8-eV band after cessation of the ArF-laser irradiation consists of two square-root time-dependent regions[15] (see Fig. 5): The first decay part corresponds to the recombination of hydrogen molecules with the E' center in the left-hand side of Eq. (1), and the second decay part corresponds to the diffusion of the hydrogen molecules. The decay curve is shown again in

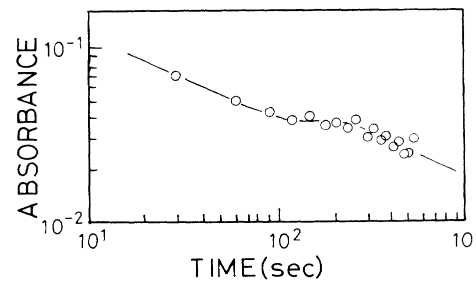


FIG. 5. Decay of the intensity of the 5.8-eV band in sample DR irradiated with the ArF excimer laser after Ref. 14.

Fig. 5. The decay of the first part is completed in about 100 sec.[15] Since the first period of the x-ray exposure is 5 min, the diffusion of the hydrogen atoms is completed in this period. Therefore, the first square-root time-dependent part of the x-ray-induced 5.8 eV band should correspond with the diffusion of the H_2 molecules. The saturated value of the absorbance of the first stage is about 0.1. The extrapolated value of the absorbance directly after cessation of the irradiation is about 0.4. This discrepancy derives from the fact that the x rays can transmit only a few millimeters from the surface of the sample.

The second stage of the square-root-dependent region in Fig. 3 seems to be derived from quite a different origin than in the case of the ArF-laser irradiation. This is supported by the fact that the 5.8 and the 4.8 eV bands are induced simultaneously by irradiation with x rays in the fused silica synthesized under an oxidizing condition, while the 5.8 eV band is not induced by irradiation with the ArF laser. The 5.8-eV band in these two kinds of samples seems to be derived from the same origin, i.e., an inherent structure of the glass network.

One might consider that the Si—O—Si strained bond in the glass network is a candidate of the precursor of the E' center:

$$\equiv \mathrm{Si{-}O{-}Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si\cdot \cdot O{-}Si} \equiv . \qquad (3)$$

If this reaction proceeds, an absorption band at 2.0 eV derived from the nonbridging oxygen-hole centers (NBOHC's; $\equiv$Si—O·) would be observed in addition to the 5.8-eV band. The NBOHC's cause an absorption band at 2.0 eV.[19] However, we did not observe the 2.0-eV band in sample DR. Therefore, this mechanism can be ruled out. The 2.0-eV band can be observed only in sample DO irradiated with the x-ray and ArF lasers. In sample DO annealed in ambient helium, the 2.0-eV band is observed by irradiating with the ArF laser but the 5.8-eV band was not induced.[16] Therefore, in sample DO, the mechanism described in Eq. (3) would not occur.

Another candidate of the precursor of the 5.8-eV band is an oxygen vacancy $\equiv$Si · · · Si$\equiv$,[20] where "· · ·" represents an unrelaxed or stretched bond. From this structure, the E' center will be produced as

$$\equiv \mathrm{Si} \cdots \mathrm{Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si}\cdot + \overset{|}{\underset{/\ \backslash}{\mathrm{Si}^+}} + e^- , \qquad (4)$$

in which $\overset{|}{\underset{/\ \backslash}{\mathrm{Si}^+}}$ represents a planar three-oxygen coordinated structure. The structure in the left-hand side causes an absorption band at 5.02 eV called the $B_2\alpha$ band.[21] The full width at half maximum (FWHM) of this band is 0.35 eV and it causes emission bands at 4.4 and 2.7 eV. There is a PLE band at 4.9 eV in the present sample. Although this band is not very different from the absorption peak of the $B_2\alpha$ band derived from the oxygen-deficient center (ODC), the FWHM of this band is about 0.37 eV and it causes PL bands at 4.3 and 2.8 eV corresponding to the emission peak excited at the $B_2\alpha$ band. To confirm this point, we compared in Fig. 6 the PL and PLE spectra in a soot remelted silica containing no OH which has the $B_2\alpha$ band.[17,18] Emission bands at 3.7 and 4.3 eV are induced by exciting with 5.0-eV photons, and a PLE peak at 4.9 eV with FWHM of 0.37 eV was observed. This fact suggests that the PLE in sample DR irradiated with x rays is derived from the $B_2\alpha$ band. The reason the 5.0-eV band is not observed in the absorption spectra is that the luminescence is more sensitive and the absorption band is hidden in the tail of the 5.8 band.

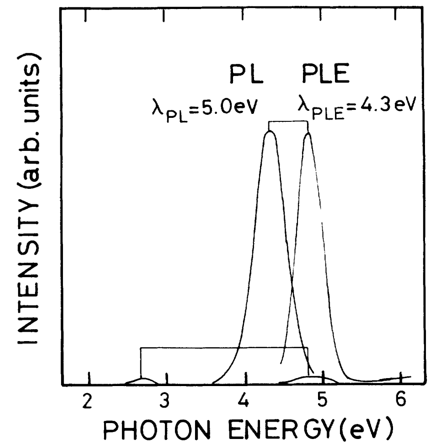


FIG. 6. Photoluminescence (PL) and photoluminescence excitation spectra of soot remelted silica with $B_{2\alpha}$ band.

In spite of this evidence of the existence of the ODC, the ODC would not be the origin of the E' center. This structure does not originally exist in the sample before x-ray exposure because (i) no $B_2\alpha$ band is observed before x-ray irradiation, and (ii) in spite of the E' center being induced by the x-ray exposure, there is no evidence of the existence of the $B_2\alpha$ band in sample DO, i.e., there are no PL and PLE bands to suggest the existence of the $B_2\alpha$ band.

In type-III silica, stoichiometrically excessive numbers of H_2O molecules are produced in the flame. Therefore, if the oxygen-deficient center $\equiv$Si · · · Si$\equiv$ is formed in the glass-formation process, this structure will react with the H_2O molecule in the flame as

$$\equiv \mathrm{Si} \cdots \mathrm{Si} \equiv + 2\mathrm{H_2O} \longrightarrow \equiv \mathrm{Si{-}OH\ \ HO{-}Si} \equiv + \mathrm{H_2} , \qquad (5a)$$

or

$$\equiv \mathrm{Si} \cdots \mathrm{Si} \equiv + \mathrm{H_2O} \longrightarrow \equiv \mathrm{Si{-}H\ \ H{-}O{-}Si} \equiv . \qquad (5b)$$

Therefore, the $B_2\alpha$ band observed by PL and PLE spectra may be formed in the process of the x-ray exposure.

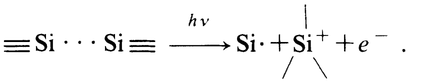
The creation of the ODC and the E' center can be explained by assuming the precursor of these defects to be the same structure as in the case of the ArF-laser irradiation[15]

$$\equiv \mathrm{Si{-}H\ \ H{-}O{-}Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si} \cdots \mathrm{Si} \equiv + \mathrm{H_2O} , \qquad (6a)$$

$$\equiv \mathrm{Si} \cdots \mathrm{Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si}\cdot + \overset{|}{\underset{/\ \backslash}{\mathrm{Si}^+}} + e^- . \qquad (6b)$$

One might suspect that the E' center is produced by $\equiv$Si—O—Si$\equiv$ as

$$\equiv\mathrm{Si{-}O{-}Si}\equiv \xrightarrow{h\nu} \equiv\mathrm{Si}\cdots\mathrm{Si}\equiv + \mathrm{O}\ , \qquad (7a)$$



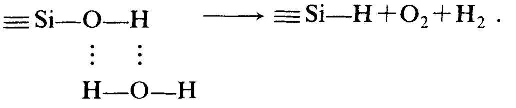
$$\equiv\mathrm{Si}\cdots\mathrm{Si}\equiv \xrightarrow{h\nu} \mathrm{Si}\cdot + \overset{|}{\underset{/\ \backslash}{\mathrm{Si}^+}} + e^-\ . \qquad (7b)$$

However this model cannot occur because the ODC does not exist in sample DO. The other candidates of the precursors of the E' center will be discussed in Sec. IV C.

B. Sample DO

The authors discussed the effects of annealing on the ArF excimer laser-induced absorption and emission bands in sample DO.[16] Irradiated with the ArF laser, an absorption band at 4.8 eV and an emission band at 1.9 eV are induced. The creation of these bands is enhanced by annealing in ambient helium. In addition to these bands, an absorption band at 2.0 eV ascribed to the NBOHC was observed in sample DO annealed in ambient helium. Annealing in ambient hydrogen, on the other hand, suppressed the creation of these bands. However, these bands will be induced again by subsequent annealing in air.

Awazu and Kawazoe[22] proposed a model to describe the creation mechanism of the 4.8- and 1.9-eV bands in fused silicas. The origin of the 4.8-eV absorption band is ozone molecules produced by reacting with O_2 molecules and O atoms produced by the photodecomposition. Their model can successfully explain the creation of these bands, however, the annealing effects cannot be explained solely by their model. The authors then proposed an additional mechanism in their model:[16] There must be a precursor to produce oxygen molecules by annealing in ambient helium. We proposed that the precursor is the H_2O molecule bounded to $\equiv$Si—OH by a hydrogen bond. By annealing, this structure will be recombined as



$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H} \\ \quad\ \ \vdots\quad\ \vdots \\ \quad\ \mathrm{H{-}O{-}H}\end{array} \longrightarrow \equiv\mathrm{Si{-}H} + \mathrm{O_2} + \mathrm{H_2}\ . \qquad (8)$$

The H_2 molecules in the right-hand side of Eq. (8) will diffuse out from glass by the annealing, and the O_2 molecules will remain in the glass network. Irradiated with the ArF laser, oxygen atoms and the NBOHC's are produced by

$$\begin{aligned}\equiv\mathrm{Si{-}H} + \mathrm{O_2} &\longrightarrow \equiv\mathrm{Si}\cdot + \mathrm{H} + 2\mathrm{O} \\ &\longrightarrow \equiv\mathrm{Si{-}O}\cdot + \mathrm{O} + \mathrm{H}\ . \qquad (9)\end{aligned}$$

In the last term of this equation, the hydrogen atom will diffuse out from the vicinity of this structure and the O atom will diffuse through the silica glass network to form an ozone molecule by reacting with an O_2 molecule trapped in the glass network.

One might suspect that the oxygen would not diffuse through the glass network. However, the O atom can diffuse into the glass network because the atomic radius (van der Waals radius)[23] of the oxygen atom (1.40 Å) is smaller than that of the helium atom (1.50 Å). The mean radius of O_2 and O_3 molecules should be greater than that of the argon atom (1.9 Å), which cannot diffuse into the glass network. Therefore, once the O_3 molecule is formed in the glass network, this molecule would be stable because no molecules diffuse to react with the O_3 molecule.

According to Eq. (9), one might be suspect that the E' center will be produced by irradiating with the ArF laser. However, because the irradiation time of the ArF laser is rather short, i.e., several minutes, most O atoms will react with the E' center as described in Eq. (9). In the case of x-ray irradiation, the irradiation time is much longer than in the case of ArF-laser irradiation, i.e., 5–180 min and the photon energy of the x rays is much larger than that of the excimer laser. Therefore, the probability of diffusing out the O atom from the vicinity of this structure will be much higher than in the case of the ArF-laser irradiation. Thus the 5.8-eV band ascribed to the E' center will be created by the x-ray exposure.

C. The other candidates of the precursors of the E' center

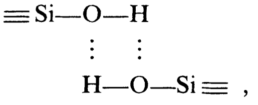
As shown above, the E' center is induced in both types of samples by x-ray exposure. We showed that the creation mechanism can be explained by assuming the same precursor as in the case of ArF-laser irradiation. However, this fact does not necessarily exclude the other mechanisms producing the E' center. In addition to the above mechanism, other mechanisms to produce the E' center can be considered, the precursors being the $\equiv$Si—O—Si$\equiv$ and $\equiv$Si—OH bases. As mentioned in Sec. IV A, the case of Si—O—Si can be ruled out.

The type-III fused silicas contain a considerable amount of OH; samples DO and DR contain 1200 and 800 ppm in weight of OH, respectively. Therefore, OH can be a candidate of the precursor of the E' center.

There are several types of OH base in vitreous silica:

(i) Single $\equiv$Si—OH ,

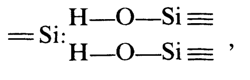
(ii)



$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H} \\ \quad\ \ \vdots\quad\ \vdots \\ \quad\ \mathrm{H{-}O{-}Si}\equiv\ ,\end{array}$$

(iii) $\equiv$Si—H H—O—Si$\equiv$,

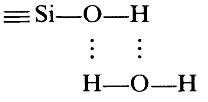
(iv)



$$=\mathrm{Si}\!:\!\begin{array}{l}\mathrm{H{-}O{-}Si}\equiv \\ \mathrm{H{-}O{-}Si}\equiv\ ,\end{array}$$

and

(v)



$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H} \\ \quad\ \ \vdots\quad\ \vdots \\ \quad\ \mathrm{H{-}O{-}H}\end{array}$$

In the following we will discuss each case.

(i) Single Si—OH. This structure is formed as a terminal of the polycondensation of $SiCl_4$ in the hydrogen-oxygen flame. Probable reaction excited by the ArF-laser irradiation is

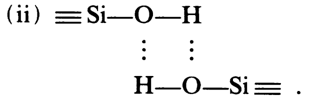
$$\equiv\mathrm{Si{-}OH} \xrightarrow{h\nu} \equiv\mathrm{Si{-}O}\cdot + \mathrm{H}\ , \qquad (10a)$$

or

$$\equiv\mathrm{Si{-}OH}\xrightarrow{h\nu}\equiv\mathrm{Si}\cdot+\mathrm{O}+\mathrm{H}\;. \tag{10b}$$

Equation (10a) is a creation of the NBOHC. The NBOHC will cause an absorption band at 2.0 eV. As shown in Fig. 2, this band does not appear in sample DR irradiated with the x-ray. Moreover, we cannot explain the creation of the ODC. Therefore, we can rule out this mechanism.

(ii)

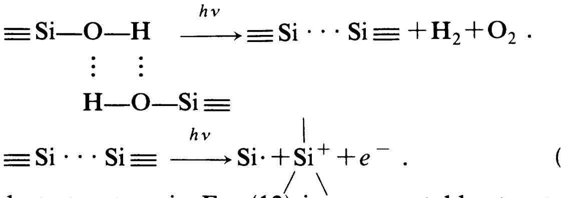


$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H}\\ \quad\;\;\vdots\quad\vdots\\ \quad\;\mathrm{H{-}O{-}Si}\equiv\;.\end{array}$$

This structure is formed by the reaction shown in Eq. (5a) or reacting Si—O—Si bonds with H_2O molecules as

$$\equiv\mathrm{Si{-}O{-}Si}\equiv+\mathrm{H_2O}\longrightarrow\equiv\mathrm{Si{-}OH\;\;HO{-}Si}\equiv\;. \tag{11}$$

In this case, a pair of OH structures will be bound by a hydrogen bond to each other. The valence electrons in the OH base will be unlocalized in this structure. Therefore, from this structure, the E' center will be produced by the following process



$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H}\xrightarrow{h\nu}\equiv\mathrm{Si}\cdots\mathrm{Si}\equiv+\mathrm{H_2}+\mathrm{O_2}\;.\\ \quad\;\;\vdots\quad\vdots\\ \quad\;\mathrm{H{-}O{-}Si}\equiv\\ \equiv\mathrm{Si}\cdots\mathrm{Si}\equiv\xrightarrow{h\nu}\mathrm{Si}\cdot+\overset{|}{\underset{/\;\backslash}{\mathrm{Si}}}{}^{+}+e^{-}\;.\end{array} \tag{12}$$

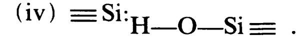
The last structure in Eq. (12) is a very stable structure. Imai and co-workers[11,12] observed the E' center in this structure by electron-spin resonance (ESR), and showed that the E' center does not tend to decay even after several days.[12] This model can explain the existence of the $B_{2\alpha}$ band in the x-ray-irradiated sample DR. The O_2 molecule in the right-hand side of the first equation of Eq. (12) causes the 4.8-eV band, derived from the O_3 molecule, or the 2.0-eV band derived from the NBOHC's. However, the ODC is only observed in sample DR irradiated with x rays and the 4.8- and the 2.0-eV bands are observed only in sample DO. Moreover, this model causes the $B_{2\alpha}$ band, which does not exist in sample DO. Therefore, this structure can be ruled out as a candidate precursor of the E' center.

(iii) ≡Si—H H—O—Si≡. This structure is formed by the reaction of Eq. (5b) or reacting ≡Si—O—Si≡ bond with H_2 molecule as

$$\equiv\mathrm{Si{-}O{-}Si}\equiv+\mathrm{H_2}\longrightarrow\equiv\mathrm{Si{-}H\;\;H{-}O{-}Si}\equiv. \tag{13}$$

As discussed in Sec. IV A , this structure exists only in sample DR.[15]

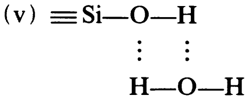
(iv)



$$\equiv\mathrm{Si}\!:\!\begin{array}{l}\mathrm{H{-}O{-}Si}\equiv\\ \mathrm{H{-}O{-}Si}\equiv\;.\end{array}$$

Existence of this structure is suggested in soot remelted silica sintered in H_2/He ambient.[24] A similar structure is reported in the grain boundary of SiO_2:GeO_2 glass[25] annealed in ambient H_2. In any case, this structure is related to the granular structure derived from the fusion of silica grandular particles. Since the type-III fused silica is grown by polycondensation of $SiCl_4$ on the surface of the ingot, the granular structure is not formed in the reaction. This structure is the origin of the $B_{2\beta}$ band causing an absorption band at 5.15 eV and emission bands at 4.2 and 3.2 eV.[21] Since this absorption band is not observed in the present samples, this structure does not exist in the present sample.

(v)



$$\begin{array}{l}\equiv\mathrm{Si{-}O{-}H}\\ \quad\;\;\vdots\quad\vdots\\ \quad\;\mathrm{H{-}O{-}H}\end{array}$$

This structure was already discussed in Sec. IV B. This structure is formed in type-III fused silica synthesized under oxidizing conditions.[16] In these silicas, O_2 molecules will be trapped in the glass network in the course of the glass formation process, and H_2O molecules will be formed by reacting with O_2 molecules trapped in the glass network. In type-III fused silica, some of H_2 molecules in the flame will diffuse into the glass during the formation process. Some of the H_2O molecules would react with the glass network by the reaction of Eq. (11). However, the other H_2O molecules will be trapped in the glass network. If a H_2O molecule is isolated from the Si—OH base, the H_2O molecules would be stable with ArF-laser irradiation. However, if a H_2O molecule is located in the vicinity of the ≡Si—OH structure, it would be bound to ≡Si—OH by the hydrogen bond.

As discussed in this section, the most probable mechanisms to produce the E' center in the present sample are as shown in Secs. IV A and IV B.

V. SUMMARY AND CONCLUSION

We studied x-ray-induced absorption and fluorescence spectra of type-III fused silicas synthesized under reducing and oxidizing conditions.

In fused silica synthesized under reducing conditions, an absorption band at 5.8 eV was induced. There are two stages of square-root time-dependent regions of the intensity of the 5.8-eV band. After irradiation with x rays for 3 h, a PL band at 4.3 and 2.7 eV, and a PLE at 4.9 eV with FWHM being 0.35 eV were observed; these bands suggest the existence of the $B_2\alpha$ band derived from the ODC (≡Si · · · Si≡). Comparing the model to describe the ArF-laser-induced absorption, we proposed a model to describe the origin of the E' center:

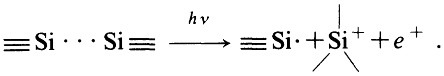
In the first step, the E' center is produced as

$$\equiv\mathrm{Si{-}H\;\;H{-}O{-}Si}\equiv\xrightarrow{h\nu}\equiv\mathrm{Si}\cdot\mathrm{H{-}O{-}Si}\equiv+\mathrm{H}$$

(diffuse out) ,

and in the second step, the E' center is created as

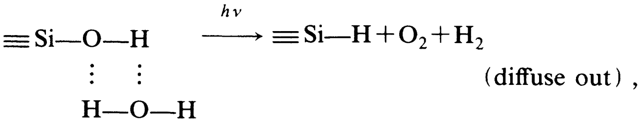
$$\equiv\text{Si—H H—O—Si}\equiv \xrightarrow{h\nu} \equiv\text{Si}\cdots\text{Si}\equiv + \text{H}_2\text{O}\ ,$$



$$\equiv\text{Si}\cdots\text{Si}\equiv \xrightarrow{h\nu} \equiv\text{Si}\cdot + \overset{|}{\underset{/\ \backslash}{\text{Si}^+}} + e^+\ .$$

These two steps correspond to the two stages of the square-root dependent region.

Absorption bands at 4.8, 5.8, and 2.0 eV are induced in the type-III fused silica synthesized under an oxidizing condition. In this sample, the $B_2\alpha$ band is not induced by irradiating with x rays. In this case these bands are created as



$$\begin{array}{l}\equiv\text{Si—O—H}\\ \quad\ \vdots\ \ \ \vdots\\ \ \ \text{H—O—H}\end{array} \xrightarrow{h\nu} \equiv\text{Si—H}+\text{O}_2+\text{H}_2\ \text{(diffuse out)}\ ,$$

$$\equiv\text{Si—H}+\text{O}_2 \xrightarrow{h\nu} \equiv\text{Si}\cdot(5.8\text{ eV abs})+2\text{O (diffusing)}\ ,$$

and

$$\equiv\text{Si—H}+\text{O}_2 \xrightarrow{h\nu} \text{Si—O}\cdot(2.0\text{ eV abs})+\text{O (diffusing)}\ ,$$

$$\text{O (diffusing)}+\text{O}_2 \longrightarrow \text{O}_3(4.8\text{ eV abs})\ .$$

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