Co-Generation of E' Center and Oxygen Hole Center in Synthetic Silica Glasses Irradiated with γ-ray

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ABSTRACT

Paramagnetic defects induced by irradiation with γ-rays in various kinds of synthetic silica glasses were studied quantitatively. The concentrations of E' center induced at room temperature agree with those of non-bridging oxygen hole center (NBOHC) in silica glasses without high amount of OH nor precursors of E' center. The concentrations of E' center induced at 77K are approximately similar to those of self-trapped holes (STHs). These results suggest that the co-generation of E' center and oxygen hole centers (OHCs), such as NBOHC or STHs, occurs as a primary process, regardless of defect generation due to pre-existing point defects.

I. INTRODUCTION

Various kinds of paramagnetic defects are generated in silica glasses by irradiation with high energy photons and electrons. Three stable defects are identified: E' center (≡Si•)[1], NBOHC(≡Si-O•)[2] and peroxy radical (POR; ≡Si-O-O•)[3] [where the symbol "≡Si" and a dot represent a silicon atom bonded to three oxygens and an unpaired electron]. Irradiation at low temperature was reported to produce unstable E' centers, self-trapped holes (STH1 and STH2), atomic hydrogen, atomic chlorine, and a triplet state[4,5]. The NBOHC, POR and STHs are categorized in OHCs. The generation mechanism of the paramagnetic defects in silica glass have also been discussed in previous works[6-12]. The subjects under discussion as regards defect generation are classified into two categories: one, the structural origin of the defects; and two, the excitation process. Although the defects are not generated by moderate irradiation in crystalline silica, the defects were found in glassy silica. Thus, glassy silica must contain the structural origin of the defects due to its amorphous structure. Pre-existing point defects[6,7] and highly disordered bond states in silica network, such as strained bonds[8,9], are proposed for the structural origin. The excitation process was suggested to be concerned with nonradiative decay of excitons[10,11], displacement of lattice oxygens, radiolysis, and trapping of free carriers[10].

In this study, the concentration of the defects induced by irradiation with γ-rays at 77K and at room temperature has been measured. A co-generation process of E' center and OHCs is discussed from the standpoint of the induced concentration and the charge neutrality.

II. EXPERIMENTAL PROCEDURE

Silica glasses were prepared from silicon tetrachloride by flame-hydrolysis, plasma oxidation, and remelting of soot preform deposited by flame-hydrolysis. Dominant defects and impurities in samples were characterized using various spectroscopies[13,14]. The preparation methods and dominant defects are listed in Table 1. Samples were irradiated with ^{60}Co γ-rays at 77K, and at room temperature. Electron paramagnetic spectra (EPR) were made to determine the concentration of paramagnetic defects, by the use of the Brucker ESP300 X-band spectrometer. The measurements were carried out at 77K. Absolute spin densities were obtained within an accuracy of 50%.

II. RESULTS

Irradiation with γ-rays at room temperature produced E' center and NBOHC in all samples, while the concentrations of E' center and NBOHC, denoted as $[E']_{RT}$ and $[NBOHC]_{RT}$, respectively, depend on samples. The dose dependences are classified into three types. As shown in Fig. 1, the dose dependences of $[E']_{RT}$ agree with those of $[NBOHC]_{RT}$ in samples S3, SF3 and SF4. Moreover, the dose dependences are almost the same for the above samples, showing sublinear growth. On the other hand, $[E']_{RT}$ is much greater than $[NBOHC]_{RT}$ in samples S2, S2H and SF1, all of which contain E'-precursors such as Si-Si, Si-H and Si-Cl. In the case of samples prepared by flame-hydrolysis, H1 and H2, $[E']_{RT}$ and $[NBOHC]_{RT}$ are relatively small at the low dose region while $[E']_{RT}$ shows the steep growth in the high dose region.

While irradiation of γ-rays at 77K produced E' center, STHs, and atomic hydrogen in all the samples, NBOHC was found only in high OH samples (H1 and H2). Induced E' center and OHCs were bleached at room temperature, thus being distinguished from stable species that were induced at room temperature. Fig.2 shows the concentration of E' center, $[E']_{77K}$, as a function of the accumulated dose. The dose dependences show linear growth and are almost the same for all samples although the concentrations in P2 and S2H are relatively large. Fig.3 shows the concentration of STHs, $[STHs]_{77K}$, in samples S2, S2H, and S3 as a function of the dose. The values of $[STHs]_{77K}$ in the other samples cannot be determined because EPR signals due to the other kind of OHCs, such as NBOHC or POR, affected that of STHs. The dose dependences of $[STHs]_{77K}$ shown in Fig.2 are approximately similar to those of $[E']_{77K}$.

IV. DISCUSSION

The values of $[E']_{RT}$ agree with $[NBOHC]_{RT}$ in samples S3, SF3, and SF4, all of which contain little amount of Si-OH and E'-precursors, such as Si-Si, Si-Cl and Si-H. This result suggests that both defects are generated at the same rate under irradiation. The fact that there are no appreciable precursors indicates that the defects originate from the silica network rather than the pre-existing point defects. The structural origin of the induced defects should be attributable to highly disordered bond states due to amorphous structure. Devine et al.[9] found the coincidence of [E'] and [NBOHC] in densified silica glasses and proposed that the cleavage of a strained bond results in co-generation of E' center and NBOHC as expressed by:

$$\equiv Si-O-Si\equiv \rightarrow \equiv Si\bullet + \bullet O-Si\equiv \quad (1)$$

The fact that $[E']_{RT}$ and $[NBOHC]_{RT}$ coincides in this study shows that the co-generation occurs even in undensified silica glasses.

In the case of irradiation at 77K, the dose dependences of $[STHs]_{77K}$ are approximately similar to that of $[E']_{77K}$. The values of $[E']_{77K}$ are almost the same for most of the samples. An analogous situation exists whthin the relationship between E' center and NBOHC generated at room temperature, whereupon it is suggested that both defects of E' center and STHs are co-generated at the same rate from disordered bond states in the silica network.

Self-trapped excitons (STE) generated at a disordered site in the amorphous structure is suggested to be changed into a defect pair consisting of E' center and interstitial oxygen[12]. Considering the results described above, E' center and NBOHC at room temperature, or E' center and STHs at 77K, quite possibly corresponds to the defect pair. Each E' center is separated by more than 30Å from other E' centers and OHCs since no distinct broadening due to spin-spin interactions is noticed in the EPR signals. In other words, the defects which are separated at sufficiently large distances from other defects remain as the only stable species. However, we have no physical reason which explains such a separation of the defect pair, especially at 77K. Thus, the large distance of the defects is explained by defect generation through STE or the cleavage of a bond only with great difficulty.

The concept of charge balance between induced defects leads to a different model. The STHs were proposed to be a hole-trapped center with STH1 and STH2 being assigned to a hole trapped on a bridging oxygen and on two bridging oxygens, respectively[5]. The condition of charge neutrality in irradiated samples should be satisfied. Although we do not know of defect states other than at paramagnetic centers, the E' center co-generated with hole-trapped center of STHs is assumed to be an electron-trapped center. Thus, trapping of electrons and holes excited by irradiation at disordered bond states is considered to be a generation process of the defects as expressed by:

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + h^{+} \rightarrow \underset{\text{(STH1)}}{\equiv\mathrm{Si{-}}\overset{\bullet +}{\mathrm{O}}\mathrm{{-}Si}\equiv} \rightarrow \underset{\text{(NBOHC)}}{\equiv\mathrm{Si{-}O}\bullet} \quad {}^{+}\mathrm{Si}\equiv \qquad (2)$$

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + e^{-} \rightarrow \underset{\text{(unstable E')}}{\equiv\mathrm{Si}\bullet \ \ {}^{-}\mathrm{O{-}Si}\equiv} \rightarrow \underset{\text{(stable E')}}{\equiv\mathrm{Si}\bullet \quad \overset{{}^{-}\mathrm{O}}{\mathrm{Si}}\equiv} \qquad (3)$$

This assumption can explain the co-generation of long-distance defects. Analogous to the pair of E' center and STHs at 77K, E' center and NBOHC at room temperature are assumed to be generated by the trapping of electrons and holes. While E' center and STHs generated at 77K bleached at room temperature, E' center and NBOHC at room temperature were stable. Thus, the unstable E' center and STHs are presumed to change into the stable E' center and NBOHC, respectively, with structural relaxation corresponding to the amount of thermal energy, as expressed by Eqs.2 and 3. The dose dependences of $[E]'_{RT}$ and $[NBOHC]_{RT}$ show sublinear growth while those of $[E']_{77K}$ and $[OHCs]_{77K}$ are approximately linear. This result suggests that the generation process at room temperature is accompanied by the annihilation process of the generated defects.

The values of $[E']_{RT}$ in samples S2, S2H, and SF1 are much larger than those in the other sample. In this case, the excess value of $[E']_{RT}$ is thought to be due to the precursors of E' center such as Si-Si, Si-H, and Si-Cl because the samples were confirmed to contain large amounts of the precursors. The values of $[E']_{77K}$ in samples S2H and SF1 are larger than those in the other samples. Thus, it is also suggested that excess concentration of E' center at 77K is due to the transformation of the precursors. However, Si-Si does not change into E' center at 77K because excess $[E']_{77K}$ was not found in sample S2. Since the change of Si-Si into E' center requires a relaxation of the network, it is presumed that the defect does not change into E' center at a low temperature. Radiolysis of Si-Cl and Si-H produces an E' center and atomic chlorine, or atomic hydrogen, without a relaxation of the network.

As for precursors of NBOHC, the Si-OH bond was proposed to be a structural origin of NBOHC as expressed by:

$$\equiv Si\text{-}OH \rightarrow \equiv Si\text{-}O\bullet + H^0 \qquad (4)$$

However, NBOHC generated at room temperature was not deduced to originate from Si-OH because $[NBOHC]_{RT}$ in H1 and H2, both of which contain a large amount of OH, was smaller than that in the other samples. The coincidence of $[NBOHC]_{RT}$ with $[E']_{RT}$ is not explained by the generation of NBOHC from Si-OH. On the other hand, NBOHC was observed at 77K only in high OH samples. Thus, the generation of NBOHC at a low temperature is suggested to be related to the existence of Si-OH.

V. SUMMARY

The concentrations of E' center induced by irradiation with γ-rays agree with those of OHCs in samples containing little amounts of pre-existing precursors. Thus, E' center and OHCs are suggested to be co-generated as a primary process of defect generation. From the standpoint of charge neutrality, one model proposes that E' center and OHCs are caused from an electron-trapped center and a hole-trapped center, respectively, at disordered bond states in the silica network. Existence of such charged states in silica glass has not been clarified as of yet. These studies, in conjunction with electrical measurements, will be help to characterize the charged defects.

In the case of samples containing precursors, additional concentration due to the transformation of the precursors is found. However, it is argued that a primary process of the defect generation is the co-generation of E' center and OHCs.

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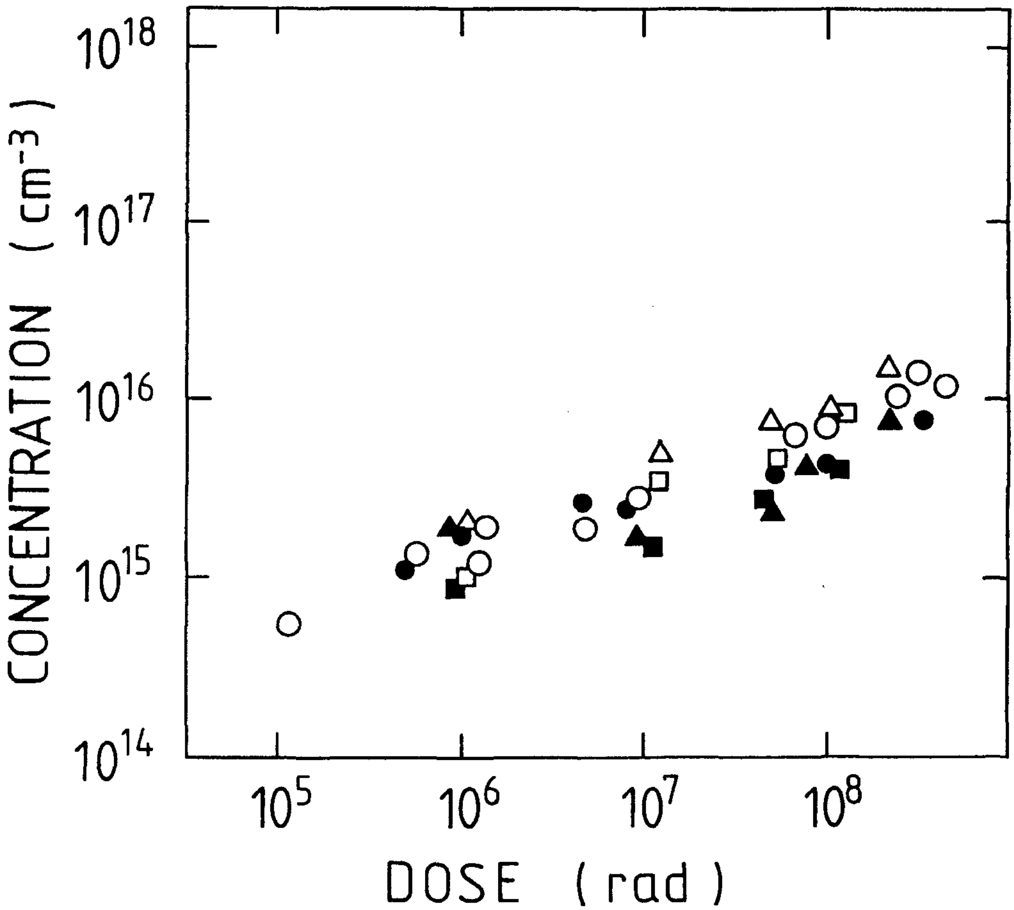

Fig.1. Concentrations of E'_{RT} in (○) S3, (△) SF3 and (□) SF4 and concentrations of $NBOHC_{RT}$ in (●) S3, (▲) SF3 and (■) SF4 as a function of accumulated dose of γ-rays irradiation at room temperature.

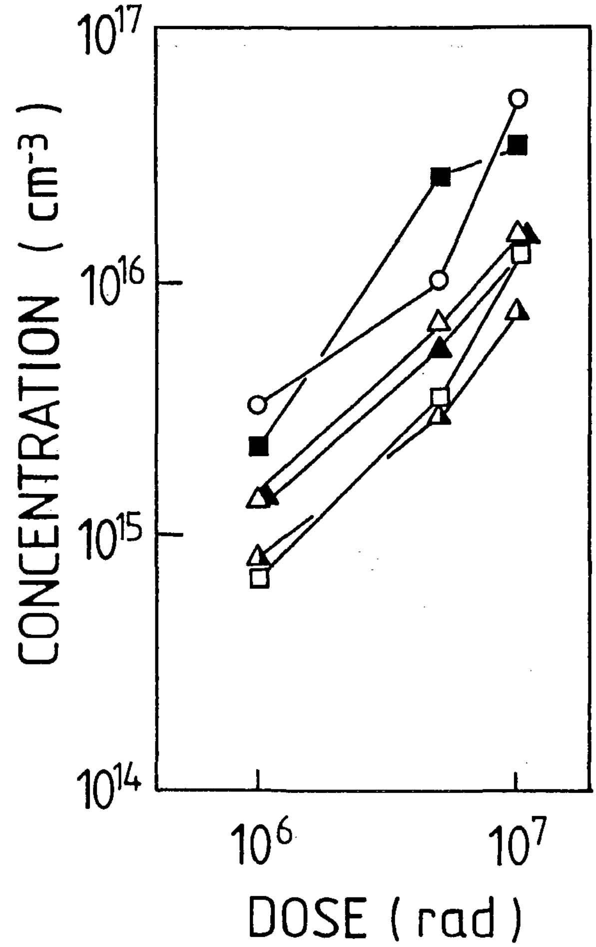

Fig.2. Concentrations of E'_{77K} as a function of accumulated dose of γ-rays irradiation at 77K in (○) P2, (△) H1, (▲) H2, (□) S2, (■) S2H and (◭) S3.

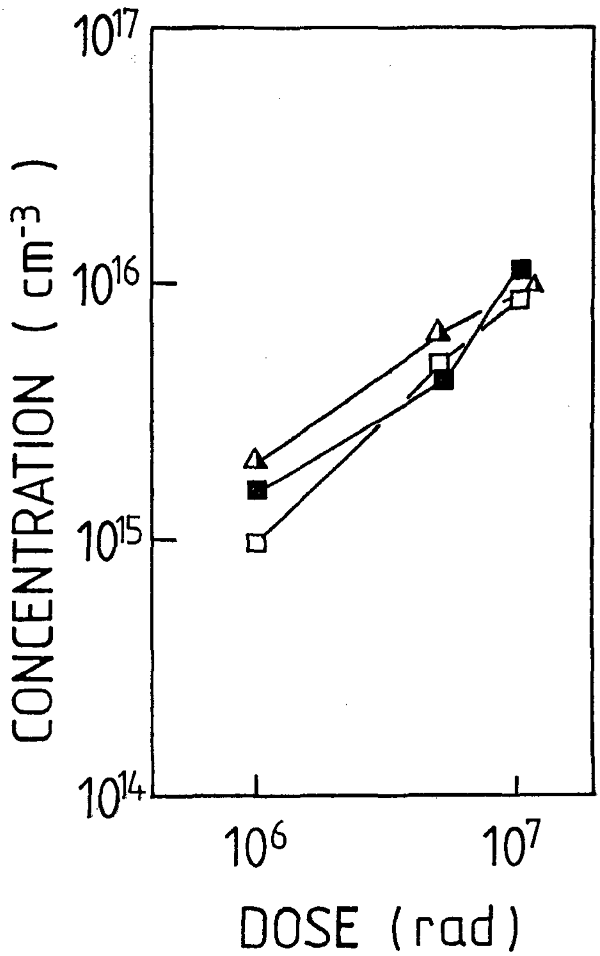

Fig.3. Concentrations of STHs as a function of accumulated dose of γ-rays irradiation at 77K in (□) S2, (■) S2H and (▲) S3.

Table 1. The Preparation History and Dominant Defects and Impurities in Synthetic Silica Glasses Used in This Study.

Sample	Preparation method	Concentration (cm^{-3}) Si-OH	Si-Si	POL*	Si-H	Cl	F
P2	O_2 plasma	nd**	nd	$3x10^{18}$	nd	$1x10^{19}$	nd
H1	Flame-hydrolysis	$4x10^{19}$	nd	nd	nd	$6x10^{18}$	nd
H2	Flame-hydrolysis	$6x10^{19}$	nd	nd	nd	nd	nd
S2	Soot-remelting	nd'	$1x10^{16}$	nd	nd	$3x10^{18}$	nd
S2H	S2 treated in H_2	nd	nd	nd	$\sim 10^{18}$	$3x10^{18}$	nd
S3	Soot-remelting	$1x10^{19}$	nd	nd	nd	$3x10^{18}$	nd
SF1	Soot-remelting	nd	nd	nd	nd	$1x10^{19}$	nd
SF3	Soot-remelting	nd	nd	nd	nd	$1x10^{18}$	$5x10^{20}$
SF4	Soot-remelting	nd	nd	nd	nd	$1x10^{18}$	$6x10^{20}$

*POL: Peroxy linkage(Si-O-O-Si) or molecular oxygen

**nd: Not detected