PHYSICAL REVIEW B VOLUME 41, NUMBER 11 15 APRIL 1990-I

Generation mechanism of photoinduced paramagnetic centers from preexisting precursors in high-purity silicas

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(Received 2 November 1989)

High-purity silicas synthesized by various manufacturing methods were studied by electron-spin resonance after being irradiated by ArF excimer laser (6.4 eV) at room temperature. E' centers ($\equiv$Si·) are induced in all samples, while nonbridging oxygen hole centers ($\equiv$Si—O·) appear only in oxygen-surplus silicas and in a sample which has an absorption band at 5.1 eV. The concentration of E' centers varies from sample to sample, ranging between 10^{14} and 10^{16} spins/cm^3 for the exposure at the average power density of 28 mJ/cm^2 per pulse at 15 Hz for 1 h. The sample dependence regarding the species and concentrations of photoinduced defects is well explained in terms of transformation of preexisting precursors to paramagnetic defects through a two-photon-absorption process.

I. INTRODUCTION

Radiation-induced paramagnetic centers in silica have been studied by electron-spin resonance (ESR) for over the past several decades.[1] Although fundamental defects such as E' center ($\equiv$Si·),[2] nonbridging oxygen hole center (NBOHC; $\equiv$Si—O·),[3] and peroxy radical ($\equiv$Si—O—O·) (Ref. 4) have been elucidated by ESR (the symbol $\equiv$Si and dot "·" represent a silicon atom bonded to three oxygens and an unpaired electron, respectively), their formation mechanisms have not been well understood.

Stathis *et al.*[5] first observed photoinduced paramagnetic defects in high-OH and low-OH silicas irradiated at room temperature by excimer lasers with photon energies of 5.0, 6.4, and 7.9 eV. Devine *et al.*[6] studied the temperature dependence of paramagnetic defect creations in low-OH silica by KrF (5.0 eV) laser irradiation. Imai and co-workers[7,8] studied the generation and the stability of E' centers in silicas with different intrinsic defects. They[9] also reported that E' centers are created through the two-photon absorption by ArF laser irradiation. Tsai *et al.*[10] proposed that E' centers are created from normal $\equiv$Si—O—Si$\equiv$ bonds by the nonradiative decay of excitons, based on the observation of E' centers as high as 10^{17} spins/g in both high–water-content (Suprasil 2) and low–water-content (Suprasil W) silicas and the absence of electron-trap nitrogen centers in ArF-laser-irradiated Suprasil 2.

We have previously reported[11] that defect species induced in pure-silica glasses by γ irradiation strongly depend on the stoichiometry, or the absolute deficiency or surplus of oxygen atoms to silicon atoms. That is to say, the lack of stoichiometry leads to the generation of either oxygen vacancies ($\equiv$Si—Si$\equiv$) or peroxy linkages ($\equiv$Si—O—O—Si$\equiv$) in as-manufactured pure-silica glasses.[11] This was confirmed by ESR observations, optical-absorption measurements, and theoretical calculations.[12,13] For example, the oxygen vacancy has optical-absorption bands at 5.0 and 7.6 eV, while the peroxy linkage has an optical-absorption band at 3.8 eV. Since the 5.0- and 3.8-eV bands do not coexist in as-manufactured silicas, oxygen vacancy and peroxy linkage are not considered to be a Frenkel defect pair. Based on this fact, we classified low-OH silicas into two types, oxygen surplus and oxygen deficient.[11–13] Also, Imai and co-workers[7–9] observed absorption bands due to peroxy linkages and OH-groups in vacuum ultraviolet region, as well as the 5.0- and 7.6-eV bands. They also proposed that especially in oxygen-deficient-type silica glasses, E' centers are created by ionization of neutral oxygen vacancies by ArF laser irradiation.

In contrast to this, it has been proposed that a close pair of transient E' center and peroxy linkage can be created by the formation of self-trapped excitons at normal $\equiv$Si—O—Si$\equiv$ sites, following the electronic excitation.[14–16] It was also suggested that these transient Frenkel defects may be transferred further into permanent defects when the density of excitation is high enough to ionize them again.[15,16]

However, little direct experimental evidence[10,17] for this mechanism of permanent E'-center generation has been reported so far. Our previous experimental observations on γ-irradiated silicas[11,13] described above suggest that such a large structural relaxation leading to the formation of Frenkel defect pair (oxygen vacancy and peroxy linkage) does not occur in the defect formation process, or if any, defects produced by such process are considered to be below our detection limit. The excitonic mechanism of E'-center generation suggests that peroxy linkages, believed to be one of the precursors of peroxy radicals, are created as the Frenkel counterpart of transient E' center. Therefore, we expect peroxy radicals to be equivalent in concentration to permanent E' centers in any types of irradiated low-OH silicas. However, this is in contrast to our previous report[11] that peroxy radicals were observed only in γ-irradiated oxygen-surplus silicas. Furthermore, a recent calculation done by Shluger[18] on the self-trapped exciton in crystalline SiO_2 shows that only a small relaxation of oxygen atom by about 0.3 Å from the normal oxygen site can be expected and supports our view.

Thus, the defect formation mechanism is still a controversial issue in the studies on photoinduced and radiation-induced defects in silica glasses. Specifically on the laser-induced defects, the correlation between the two-photon process and defect generations seems to be established, as previously described. But, so far, to our knowledge, no explanation has been given on how the two-photon-absorption process will lead to the defect generations.

This report presents evidence that defects induced by ArF laser irradiation are created from preexisting precursors due to the nonstoichiometry, such as oxygen vacancies and peroxy linkages. The use of well-characterized silicas mentioned above gives us sufficient information on the correlation between preexisting precursors in as-manufactured silicas and paramagnetic centers induced by ArF laser irradiations. We also discuss several kinds of mechanisms involving the transformation of preexisting precursors to paramagnetic centers following the two-photon-absorption process.

II. EXPERIMENTAL PROCEDURE

Various properties of samples used in the present study are shown in Table I. The samples are classified into "high-OH" or "low-OH" silica. Low-OH silicas are further classified into "oxygen deficient" or "oxygen surplus." Oxygen-deficient silica glasses exhibit the 5.0-eV (referred to as the $B_2\alpha$ band) and 7.6-eV bands, reported to be due to neutral oxygen vacancies,[12] while oxygen-surplus silicas have the 3.8-eV absorption band caused by peroxy linkages.[13]

The optical absorption between 200 and 800 nm was measured on 10-mm-diam rods with a length 40–45 mm. Peak values of typical optical-absorption bands in optical density (OD/cm) are shown in Table I. Samples for ArF excimer laser irradiation are polished plates of 0.7 mm thickness cut into several pieces with dimension of 25 mm×2 mm. An area of 10 mm^2 was exposed to the unfocused beam from a multigas excimer laser (Lumonics Hyper EX-400) with ArF as the lasing medium at room temperature for 1 h at 15 Hz. During irradiations, the output of ArF excimer laser was monitored with Scientech Calorimeter (38-2UV5), and the average power densities were estimated to be 28 mJ/cm^2 per pulse.

ESR measurements were performed at 77 K with a JEOL JES-RE2XG spectrometer operating at X-band frequency ($\nu \simeq 9.25$ GHz) and at modulation amplitude of 0.63 G. Nonsaturating microwave power was employed (5 mW for NBOHC's and 1 μW for E' centers) to record each spectrum.

TABLE I. Sample list (ND is an acronym for not detected).

Sample[a] name	Category	Manufacturing method	Impurity (ppm) Cl	OH	UV absorption bands (OD/cm) 5.0 eV[b] ($B_2\alpha$)	5.1 eV[b] ($B_2\beta$)	3.8 eV[c]
P3F	Oxygen surplus	Ar+O_2 plasma	370	0.46	ND	ND	0.018
SA2	Oxygen deficient	Ar plasma	3200	0.75	0.114	ND	ND
SB1	Oxygen deficient	O_2 plasma	1200	ND	0.034	ND	ND
SF1	Unknown ($B_2\beta$)	Soot	0.3	270	ND	0.004	ND
OH1	High OH (oxygen deficient+OH)	O_2 plasma +OH	310	200	ND	ND	ND
AH1	High OH (oxygen deficient+OH)	Ar plasma +OH	1600	20	ND	ND	ND
AH2	High OH (oxygen deficient+OH)	Ar plasma +OH	690	300	ND	ND	ND
AH3	High OH (oxygen deficient+OH)	Ar plasma +OH	340	500	ND	ND	ND
D17	High OH	Direct	76	701	ND	ND	ND
DF8	High OH	Direct	free	1000	ND	ND	ND

[a] The sample names are arbitrary designators.

[b] See Ref. 12.

[c] See Ref. 13.

III. RESULTS AND DISCUSSION

A. Sample dependence of paramagnetic defects

Figure 1 shows typical ESR spectra after ArF laser irradiation. The resonance of E' centers at $g \simeq 2.001$ is seen in all the spectra. Features at $g \simeq 2.01$ seen in (a) P3F and (b) SF1 are considered to be part of the resonance of NBOHC's. A two-line spectrum with a separation of 13.3 mT observed in (d) DF8 was reported to be due to formyl radical ($H\dot{C}O$).[19]

One of the striking features of these spectra is the lack of the resonance of NBOHC's in the high-OH silicas (DF8 and D17), while it can be observed in low-OH oxygen-surplus P3F, and SF1 which displays an optical-absorption band at 5.1 eV (referred to as the $B_2\beta$ band[12]). A second interesting result is the absence of peroxy radicals, a distinctive feature of γ-irradiated oxygen-surplus silicas,[13] in P3F after ArF laser irradiation.

The number of each paramagnetic center was calculated by comparing the result of double numerical integration of each spectrum with the JEOL strong or weak pitch standard. The results are shown in Fig. 2. It should be noted that the relative spin densities were obtained in an accuracy of $\simeq \pm 10\%$, while the absolute spin densities in an accuracy of $\simeq \pm 50\%$. The concentrations of E' centers vary from sample to sample; $\simeq 10^{16}$ spins/cm^3 were induced in AH1-3 and OH1, while 1 or 2 orders of magnitude lower in the other samples.

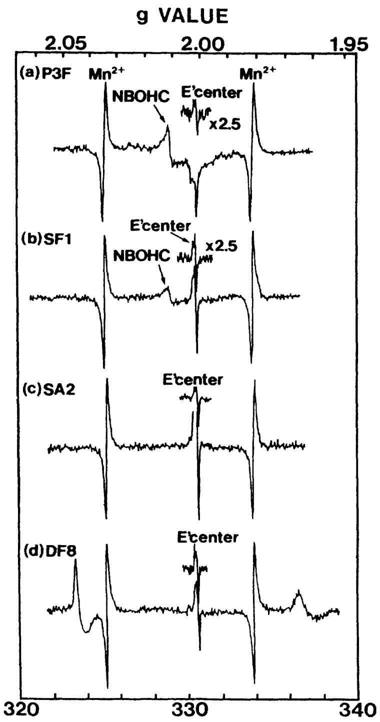

FIG. 1. ESR spectra of (a) oxygen-surplus P3F, (b) SF1 with $B_2\beta$ band, (c) oxygen-deficient SA2 with $B_2\alpha$ band, and (d) high-OH DF8, after ArF laser irradiation. Spectra were obtained at 77 K and X band ($\nu \simeq 9.25$ GHz) under nonsaturating conditions (1 μW for E' centers and 5 mW for NBOHC's and formyl radicals). Features at $g = 1.981$ and 2.034 in each spectrum are due to Mn^{2+} for g-value calibration.

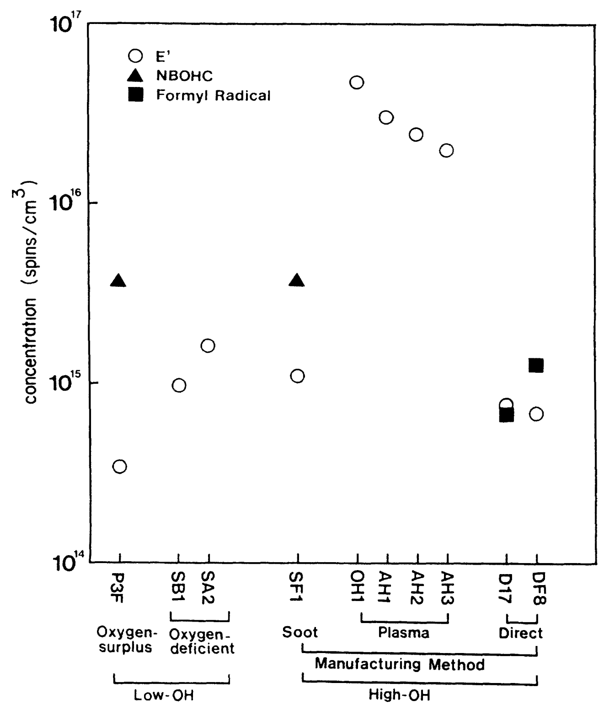

FIG. 2. Concentrations of paramagnetic centers (○, E' centers; ▲, NBOHC; ■, formyl radical) induced by ArF laser irradiation in low-OH (oxygen-surplus P3F, oxygen-deficient SA2 and SB1), SF1 which exhibits $B_2\beta$ band, and high-OH (OH1, AH1, AH2, and AH3, DF8, and D17).

The strong sample dependence of defect species and populations suggests that the defect-generation mechanism by ArF laser is due to the transformation of precursors. The idea is consistent with our previous studies on γ-irradiated silicas.[11]

B. Defect-generation mechanism: energy transfer to precursors

The energy levels of various defects in amorphous SiO_2 calculated by O'Reilly and Robertson are shown in Fig. 3.[20,21] Since the energy separations between the conduction-band edge and the highest occupied levels of these defects are higher than the one-photon energy of an ArF laser (6.4 eV), a possible mechanism of defect formation is a two-photon process, as proposed by Arai *et al.*[9] In fact, ArF laser power used in the present study ($\simeq 28$ mJ/cm^2 per pulse) is in the region where the growth of E' centers is reported[9] to be proportional to the square of the laser-pulse energy per unit area.

Since ArF-laser-induced defects show sample dependence as discussed in Sec. III A, the defect generation by ArF laser is considered to be due to the transformation of precursors to paramagnetic centers. Thus, the following defect-formation processes involving the two-photon absorption are possible: (i) two photons are directly absorbed by the excitation of preexisting precursors, which are then transformed into paramagnetic centers, and (ii) electron-hole pair or exciton formation by the excitation of electrons from the upper valence band through two-photon absorption, and subsequent energy transfer from electron-hole pairs or excitons to precursors. The upper valence band consists of nonbonding and weakly bonding states of normal $\equiv$Si—O—Si$\equiv$ bonds.[21] Since, the electron concentration in the upper valence band is much higher than preexisting precursors such as $\equiv$Si—Si$\equiv$ and $\equiv$Si—O—O—Si$\equiv$, the latter case (ii) is considered to be dominant in the two-photon absorption. This is supported by the results of Mizunami *et al.*[22] who measured two-photon-absorption coefficients at 282 nm (4.4 eV) using high-OH and oxygen-deficient-type pure-silica core fibers and obtained the same value of 5×10^{-6} cm/MW for both types of fibers.

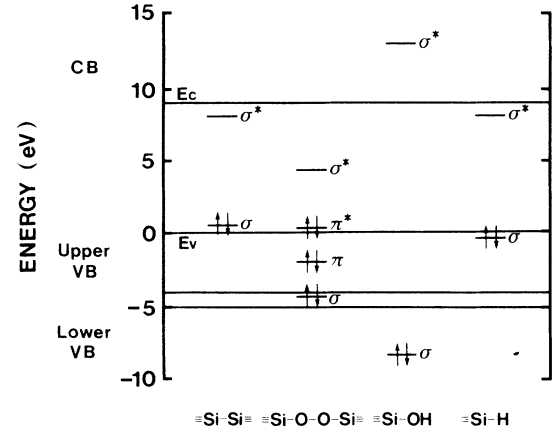

FIG. 3. The energy diagram of various nonparamagnetic centers in normal $\equiv$Si—O—Si$\equiv$ network proposed by O'Reilly and Robertson (after Refs. 20 and 21). The upper valence band lying at -4–0 eV consists of the nonbonding states and the weakly bonding states of normal $\equiv$Si—O—Si$\equiv$ bond, and the lower valence band lying below at -5 eV consists of the strong bonding states.

The defect-formation mechanism here can be schematically expressed by a series of the following reactions:

$$\equiv\text{Si—O—Si}\equiv\ +2h\nu\rightarrow(\equiv\text{Si—O—Si}\equiv)^*\ , \tag{1a}$$

$$(\equiv\text{Si—O—Si}\equiv)^*+(\text{precursor})\rightarrow\ \equiv\text{Si—O—Si}\equiv\ +(\text{precursor})^*\ , \tag{1b}$$

and

$$(\text{precursor})^*\rightarrow(\text{paramagnetic center})\ . \tag{1c}$$

Here, $h\nu$ denotes a single photon, and the asterisk "$*$" means the excited state. Specifically, the $(\equiv$Si—O—Si$\equiv)^*$ represents a mobile electron-hole pair or exciton delocalized over the $\equiv$Si—O—Si$\equiv$ network. Further discussion on the excited states is beyond the scope of this paper. The reaction (1b) shows that the excited states, whether in the forms of electron-hole pairs or excitons, transfer energies of 9 to 13 eV to precursors when they recombine. In the reaction (1c), subsequent bond cleavage or ionization results in the creation of paramagnetic center.

In the case of irradiation by 7.9-eV photons (F_2 excimer laser), or by higher-energy photons such as x rays or γ rays, the excitation of an electron from much lower valence band, or inner core levels, can be expected. In these cases, it is possible that defect species not observed by 6.4-eV laser irradiation are created. From this viewpoint, the difference in defect species between the case of irradiation by ArF laser, and by higher-energy photons (e.g., the generation of a NBOHC from $\equiv$Si—OH, and that of peroxy radical from peroxy linkage) will be discussed in the following sections.

C. Precursors of NBOHC's

We first discuss the generation mechanism of NBOHC's. Since peroxy linkages are presumably dominant defects in oxygen-surplus P3F,[13] it is suggested that NBOHC's are created through the fission of O—O bonds:

$$\equiv\text{Si—O—O—Si}\equiv\ \rightarrow\ \equiv\text{Si—O}\cdot\ +\ \cdot\text{O—Si}\equiv\ . \tag{2}$$

This mechanism is possible, since according to Fig. 3, the energy splitting between σ and σ^* orbitals ($E_{\sigma-\sigma^*}$) of O—O bond of peroxy linkage is $\simeq$9.4 eV, that is lower than the absorbed two-photon energy of 6.4-eV light. A puzzling result that NBOHC's are absent in high-OH silicas can be interpreted in the following way. The $E_{\sigma-\sigma^*}$ of ($\equiv$Si—) O—H bond of about 20 eV is much higher than the two-photon energy. Therefore, we cannot expect the dissociation of O—H bond:

$$\equiv\text{Si—OH}\ \rightarrow\ \equiv\text{Si—O}\cdot\ +\ \cdot\text{H}\ . \tag{3}$$

Tsai *et al.*[23] assumed that the reaction (3) occurs based on his experimental results of ArF laser irradiation with the average pulse power density of 120 mJ/cm^2. The discrepancy between their results and ours can be explained as follows. According to the density of states of $\equiv$Si—OH calculated by Robertson[21] (not shown in Fig. 3), the σ and σ^* orbitals have weak tails toward the valence- and conduction-band edges, respectively. This may make it possible that a small fraction of $\equiv$Si—OH may be dissociated into NBOHC's and atomic hydrogens by ArF laser irradiation. In this case, the reaction yield is considered to be small and depends on the laser power density. The induced NBOHC's are presumed to be under the detection limit in the present study. Another possibility is that the reaction (3) is caused by the three-photon-absorption process. This will be discussed in detail later, but again the reaction yield must strongly depend on the laser power density. In the case of γ irradiation, since the generation of electron-hole pairs or excitons with energies of more than 20 eV from lower valence band is possible, NBOHC's are considered to be generated according to reaction (3).

Interestingly, NBOHC's are also observed in SF1, which has the $B_2\beta$ band. Because NBOHC's are only observed in SF1 except in oxygen-surplus P3F, the defects responsible for the $B_2\beta$ band are considered to be the precursors of NBOHC's. Skuja *et al.*[24] ascribed this band to germanium impurity. In our case, however, the sample SF1 is a high-purity synthetic silica. Therefore, we ruled out the Ge-impurity model. Kohketsu *et al.*[25] also observed the $B_2\beta$ band in SiO_2 glasses sintered under the reducing atmosphere (the mixture of hydrogen and helium gas) in the preparation by the vapor-phase axial deposition (VAD) method, and attributed the $B_2\beta$ band to two-fold coordinated silicon

$$(\mathrm{O{-}\overset{\cdot}{\underset{\cdot}{Si}}{-}O})\ .$$

However, it was previously reported[26] that the $B_2\beta$ band is associated with both hydrogen and excess oxygen. Thus, a more likely candidate for the structure of the precursor of the NBOHC is $\equiv\mathrm{Si{-}O{-}O{-}H}$ in analogy with the reaction (2), rather than the two-fold-coordinated silicon model. In this case, the NBOHC can be produced by breaking the weak O—O bond:

$$\equiv\mathrm{Si{-}O{-}O{-}H} \rightarrow \equiv\mathrm{Si{-}O\cdot} + \cdot\mathrm{OH}\ , \qquad (4)$$

We speculate here that the $B_2\beta$ band may arise from the transition of the diamagnetic state at the O—O bond, specifically $\pi^* \rightarrow \sigma^*$ transition, likewise the case of the 3.8-eV band caused by peroxy linkage,[13] as shown in Fig. 3.

D. Precursors of E' centers

Next, we turn to generation of E' centers. As shown in Fig. 3, the energy of electron-hole pair or exciton (9–13 eV) is sufficient to excite an electron in the σ orbital of $\equiv\mathrm{Si{-}Si}\equiv$ to the conduction band. In this way, E' centers can be created through ionization of neutral oxygen vacancies, as predicted by theoretical calculations of Feigl, Fowler, and Yip;[27]

$$\equiv\mathrm{Si{-}Si}\equiv \rightarrow \equiv\mathrm{Si\cdot} + \mathrm{Si}\equiv + e^-\ . \qquad (5)$$

From this mechanism, the oxygen vacancy seems to be the predominant precursor in oxygen-deficient silica. However, if it is assumed that this is the only mechanism to produce E' centers in any types of silicas, it cannot explain the result that the concentration of E' centers induced in AH1-3 and OH1 is 1 or 2 orders of magnitude higher than in oxygen-deficient silica SA2. Therefore, we argue that there are different precursors of E' centers with higher efficiency of transformation than oxygen vacancies. AH1-3 and OH1 were synthesized by Ar and O_2 plasma method, respectively, with various OH content (20–500 ppm), and they have no $B_2\alpha$ band. Previous studies have shown that our samples synthesized by the same manufacturer with Ar or O_2 plasma methods without OH addition were found to be all oxygen-deficient type, exhibiting the $B_2\alpha$ band,[13] and that they can be easily terminated by hydrogen treatment at 600 °C, for 12 h.[28] From these facts, it is probable that the oxygen vacancies in AH1-3 and OH1 exist in the form of $\equiv\mathrm{Si{-}H}$ pairs as a result of the following reaction such as,

$$\equiv\mathrm{Si{-}Si}\equiv\ + \mathrm{H_2} \rightarrow\ \equiv\mathrm{Si{-}H} + \mathrm{H{-}Si}\equiv\ . \qquad (6)$$

Since the $E_{\sigma-\sigma^*}$ of a $\equiv\mathrm{Si{-}H}$ bond is about 8 eV as shown in Fig. 3, the dissociation of this bond is possible:

$$\equiv\mathrm{Si{-}H} \rightarrow\ \equiv\mathrm{Si\cdot} + \cdot\mathrm{H}\ . \qquad (7)$$

The resulting atomic hydrogen can diffuse away, because of the high diffusivity, and probably react with another atomic hydrogen to form molecular hydrogen. The reverse reaction of Eq. (7) is presumed to be negligibly small and does not affect the generation of E' centers during laser irradiation, because the density of excitation is so high that the dissociation surpasses the recombination. This view is consistent with the results of Imai *et al.*[7] that the concentrations of E' centers induced in hydrogen-treated oxygen-deficient silicas is 1 order of magnitude higher than that in nontreated ones. Although the exact concentration of $\equiv\mathrm{Si{-}H}$ has not yet been determined in AH1-3 and OH1 because of the difficulty in detecting the $\equiv\mathrm{Si{-}H}$ by infrared absorption, the density of $\equiv\mathrm{Si{-}H}$ can be estimated to be at least of the order of 10^{18} cm^{-3} from the concentrations of the E' centers and oxygen vacancies observed in oxygen-deficient silica.[7]

The density of induced E' centers in high-OH samples DF8 and D17 is 2 orders of magnitude lower than those of high-OH samples OH1 and AH1-3, as shown in Fig. 2. The difference in E'-center concentrations among these samples can be ascribed to the difference in concentration of precursors between silicas synthesized by direct method (DF8 and D17) and those produced by plasma method (OH1 and AH1-3). That is, the concentration of $\equiv\mathrm{Si{-}H}$ may be lower in DF8 and D17 than that in OH1 and AH1-3.

E. Effects of laser power density and precursors on E' center concentrations

In contrast to the present observation, Tsai *et al.*[10] reported that E' centers as high as 10^{17} spins/g were induced by ArF laser irradiations in both high–water- and low–water-content silica. Based on this, they suggested that these E' centers are not induced through the ionization of preexisting oxygen vacancy, and that they must be created from normal $\equiv\mathrm{Si{-}O{-}Si}\equiv$ bonds through nonradiative decay of excitons. More recently, they found[29] that the laser beam was much more strongly focused than they originally stated and estimated the power density to be much higher than 120 mJ/cm^2 per pulse. Furthermore, they determined that E'-center spin densities were also 1–2 orders of magnitude higher than 10^{17} spins/g. In this way, Tsai *et al.* ascribed the much higher E' concentration than the present case to the high laser power density achieved by focusing the laser beam.

Thus, the main reason for the discrepancy in the E'-center concentration between their result and the present one seems to be the fact that our laser power density (28 mJ/cm^2 per pulse) is 1 or 2 orders of magnitude smaller than the density used by them. Therefore, it is possible that they observed E' centers created through multiphoton processes involving more than two photons only achieved by high-power-density irradiation in defect formations. This view is supported by the fact that Tsai *et al.* observed a large number of NBOHC's not only in oxygen-surplus Suprasil W, but in high-OH Suprasil 2.[23] This can be explained by assuming that the dissociation of O—H bond occurs by multiphoton process involving more than two photons according to reaction (3).

Of course, some parts of E' centers observed by Tsai *et al.* are due to the two-photon process. They reported[10] that the E'-center production efficiency in high–water-content silica is 5 to 10 times of that in low–water-content silica. This can be reasonably explained by supposing that some parts of the E' centers were created from precursors with different efficiency of transformation to E' centers.

Devine supported[17] the defect-formation mechanism of the E' centers from normal $\equiv$Si—O—Si$\equiv$ bonds due to the nonradiative decay of excitons,[10] based on the linear relationship between the E' concentration and the number of electron-hole pairs in the case of ^{60}Co γ irradiation. However, Devine's result is also explainable in our view, where paramagnetic centers are presumed to be created by the energy transfer from electron-hole pairs or excitons to precursors.

F. Absence of peroxy radicals in oxygen-surplus silica

Finally, we discuss the reason for the absence of peroxy radicals in ArF-laser-irradiated oxygen-surplus P3F. If it is assumed that the $\equiv$Si—O bonding energy of peroxy linkage is almost the same as that of $\equiv$Si—O—Si$\equiv$ bond, the threshold energy to break the $\equiv$Si—O bond in peroxy linkage is about 14 eV, the energy difference between the bottom of the conduction band and the top of the lower valence band. Thus, the cleavage of the $\equiv$Si—O bond by the two-photon energy of 6.4-eV light is impossible. On the other hand, since the two-photon energy of 7.9-eV light (15.8 eV) can excite an electron from the lower valence band, the generation of a peroxy radical from peroxy linkage can be expected by 7.9-eV laser irradiation. This picture is consistent with the results of Stathis *et al.*[5] who reported that part of peroxy radicals at $g \simeq 2.007$ was observed in F_2-laser (7.9 eV) irradiated Suprasil W, while not in ArF-laser (6.4 eV) irradiated one. Previous observation of peroxy radicals in γ-irradiated oxygen-surplus silicas[13] can be explained in terms of the excitation of electrons from the lower valence band.

IV. SUMMARY

It is clearly demonstrated that the strong sample dependence of paramagnetic species and concentrations exists in silicas prepared under different conditions with different manufacturing methods. The sample dependence can be explained in terms of the transformation of various nonparamagnetic precursors in as-manufactured silica glasses. The energy for the transformation of precursors to paramagnetic defects is presumed to be provided by the recombination of electron-hole pairs or excitons, created through the two-photon-absorption process. Since electron-hole pairs or excitons, produced by the excitation of an electron from the upper valence band can emit the energy of about 9–13 eV when they recombine, the generation of E' centers from $\equiv$Si—Si$\equiv$ and $\equiv$Si—H and that of NBOHC's from $\equiv$Si—O—O—Si$\equiv$ can be expected by ArF laser irradiation. The generation of peroxy radicals in 7.9-eV laser-irradiated oxygen-surplus silica (Ref. 5), and the absence of peroxy radicals in our 6.4-eV laser-irradiated oxygen-surplus silica can be explained by the formation of electron-hole pairs or excitons from the lower valence band, with sufficient energy (15.8 eV) to break the $\equiv$Si—O bond of peroxy linkages. In the case of multiphoton processes involving more than two photons of 6.4-eV light, or the case of higher-energy photons such as x rays or γ rays, the generation of NBOHC's from $\equiv$Si—OH is also possible, because of the ability to excite electrons from a much lower valence band. Thus, the dominant defect-formation mechanism in the present study can be interpreted as the transformation of preexisting precursors, rather than a mechanism involving the nonradiative decay of the self-trapped exciton.

ACKNOWLEDGMENTS

We acknowledge Dr. Griscom for his valuable discussion. Samples P3F, SF1, D17, and DF8 were provided by the courtesy of Shin-Etsu Quartz Products Co., Ltd., and Shin-Etsu Chemical Co., Ltd. This work was partly supported by a Grant-in-Aid for General Scientific Research (No. 01460143) from the Ministry of Education, Science and Culture of Japan, and by the Tokyo Electric Power Company (TEPCO) Research Foundation.

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