# Characterization of ClO<sub>x</sub> radicals in vacuum-ultraviolet-irradiated high-purity silica glass

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An electron-spin-resonance (ESR) study was made on the defect centers induced by vacuum-

ultraviolet (vuv) laser (7.9-eV) irradiation in high-purity silica glasses. We observed two types of ESR spectra, each consisting of a concentric pair of four-line peaks, in low-OH oxygen-surplus silica produced with plasma methods. Spin-Hamiltonian parameters determined by computer simulation of the experimental ESR line shapes are consistent with oxy-radicals of chlorine. The observed  $ClO_x$  (x = 2, 3) radicals are considered to be due to the reaction between chlorine and oxygen, which were both produced by vuv-laser irradiation.

#### I. INTRODUCTION

Impurities in silica glass such as transition-metal ions and hydroxyls affect the optical transmission of the material.<sup>1</sup> Thorough elimination of hydroxyl has been found to be critical in the final development of low-loss optical fiber with 0.2 dB/km absorption loss at the wavelength of 1.55  $\mu$ m. High-purity silica is generally produced by flame hydrolysis (type III) or plasma oxidation (type IV) of SiCl<sub>4</sub>. In the VAD (vapor-phase axial deposition) process, SOCl<sub>2</sub> and Cl<sub>2</sub> gases are used as a dehydration reagent.<sup>1</sup> Therefore, chlorine is a common impurity abundant (about ten to several thousands ppm) even in the so-called "high-purity" silica.

Recently, high-purity silica glass also attracts much attention as a material for ultraviolet (uv) -grade optics for excimer-laser applications. Several reports showed that irradiation with intense uv light from excimer lasers results in the activation of defect precursors<sup>2-5</sup> or the bond breaking of normal Si-O-Si networks.<sup>6</sup> A nitrogen center was observed in some types of commercially available silica (Suprasil 1 or 2) irradiated with 7.9-eV excimer laser<sup>2</sup> or x-ray.<sup>7</sup> A reaction of hydroxyls has been reported to lead to the production of nonbridging-oxygen hole centers (NBOHC's,  $\equiv$ Si-O·) and atomic hydrogens (H<sup>0</sup>) in a high-OH silica irradiated with 6.4-eV laser:<sup>8</sup>

$$\equiv \text{Si-OH} \rightarrow \equiv \text{Si-O} \cdot + \text{H}^0 . \tag{1}$$

Here, the symbol  $\equiv$  and the dot denote a bonding with three separate oxygens and an unpaired spin, respectively. Despite fairly large concentrations of impurity chlorine in some high-purity silicas, on the other hand, the behavior of chlorine during or after uv-excimer-laser irradiation is not well understood.

To date, three chlorine-related paramagnetic species,

atomic chlorine (Cl<sup>0</sup>), Cl<sub>2</sub><sup>-</sup>, and the  $E'_{\delta}$  center have been reported in x-irradiated silica. Griscom and Friebele<sup>9</sup> observed atomic chlorine and  $E'_{\delta}$  centers in x-irradiated high-purity silica. Griscom, Friebele, and Mukherjee<sup>10</sup> reported Cl<sub>2</sub><sup>-</sup> radicals in an x-irradiated silica synthesized with sol-gel method.

In this report, we made an electron-spin-resonance (ESR) study on a series of high-purity silica glasses irradiated with excimer laser of a photon energy of 7.9 eV. We found the spectrum in the low-OH oxygen-surplus silica after 7.9-eV laser irradiation. The spectrum is found to be a superposition of two spectra, each exhibiting a fourline structure, which are due to hyperfine interaction with nuclei having spin  $I = \frac{3}{2}$ . Computer line-shape simulation revealed that these spectra are due to two types of  $ClO_x$  radicals (x = 2, 3). The formation mechanism of these radicals is also discussed.

#### **II. EXPERIMENTAL PROCEDURES**

Samples used in the experiments are high-purity silica glasses manufactured by plasma oxidation (Ar or  $Ar+O_2$ plasma) or flame hydrolysis (direct) of SiCl<sub>4</sub>. Table I shows the classification of samples based on the oxygen stoichiometry,<sup>5</sup> OH concentration, manufacturing methods, and concentration of impurities such as hydroxyl and chlorine. The samples were strips with dimensions of  $1 \times 2 \times 25$  mm<sup>3</sup>. These were exposed to a beam from an excimer laser (Lambda Physik, LPX105i) with F<sub>2</sub>-He mixture (157 nm, 7.9 eV) at room temperature. The optical path to the sample was purged with N<sub>2</sub> gas, in order to prevent the absorption of 7.9-eV photons by oxygen. Laser power was estimated to be 3 mJ/cm<sup>2</sup> using a Scientech Calorimeter (38-2UV5). A KrFexcimer laser (Lumonics, Hyper EX-400, 248 nm, 5.0 eV)

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TABLE I. Sample list.					
Sample	Category	Manufacturing method	Impurities Cl	(ppm) OH	
1	Oxygen-surplus	$Ar + O_2$ plasma	370	0.46	
2	Oxygen-deficient <sup>a</sup>	Ar plasma	400	3.3	
3	High-OH	Direct	76	701	

TABLE I. Sample list.

<sup>a</sup>The sample has a spatial distribution in oxygen content. The center is oxygen deficient and the edge is oxygen surplus (see Ref. 13).

was employed for photobleaching experiments.

ESR measurements were carried out at 77 K with a JEOL RE-2XG spectrometer operating at X band (v=9.2-9.3 GHz). Spectra were recorded at a microwave power of 1 $\mu$ W for E' center and 5 mW for other species. Field modulation of 0.063 mT was employed for all measurements. The g values of the defect centers were determined with respect to those of the E' center, which was observable in all the irradiated samples. Isochronal thermal annealing was done in air by keeping samples in an electric furnace for 10 min in steps of 100 up to 600 °C.

# **III. RESULTS AND DISCUSSION**

Figure 1(a) shows a first derivative ESR spectrum of the oxygen-surplus sample 1 observed after 7.9-eV laser irradiation. The E' center ( $\equiv$ Si·) and the peroxy radical ( $\equiv$ Si-O-O·) are observed in the oxygen-surplus silica. In addition, it exhibits ESR signals which were not previously reported, as shown in Fig. 1 (indicated by arrows as components A, B, C, and D). For comparison, the ESR spectrum of the oxygen-deficient sample 2 after 7.9-eV laser irradiation is shown in Fig. 1(b). In the following, attention will be focused on the characterization of paramagnetic centers responsible for the components A, B, C, and D, which are observed in sample 1.

### A. Spectra associated with chlorine impurities

The ESR spectrum of sample 1 recorded at an expanded field scale is shown in Fig. 2. A fairly well-resolved spectrum was obtained for the components A and D. The "stick diagram" shown in Fig. 2 indicates that the components A and D are parts of an equally-spaced four-line structure (referred to as spectrum A). This suggests that the defect responsible for the spectrum A undergoes a hyperfine interaction with an  $I = \frac{3}{2}$  nucleus.

As for the component B, it was difficult to obtain the whole spectrum due to the overlap with the spectrum from the peroxy radicals. Hosono and Weeks<sup>11</sup> reported on a selective photobleaching of peroxy radicals by KrF-excimer laser (5.0 eV) irradiation. The following irradiation with a 5.0-eV laser (10 Hz, 15 min,  $\approx 20 \text{ mJ/cm}^2$  per pulse) was made on the sample 1, in order to resolve the features associated with the component B. Figure 3 shows ESR spectra obtained before and after the 5.0-eV laser irradiation. The component B grows as the spectrum due to peroxy radicals disappears. Consequently, it



MAGNETIC FIELD (mT)

FIG. 1. ESR spectrum obtained for (a) oxygen-surplus sample 1 and (b) oxygen-deficient sample 2, after 7.9-eV laser irradiation at 3 mJ/cm<sup>2</sup> per pulse and 50 Hz, for 55 min and 10 min at room temperature, respectively. Spectra were recorded at 77 K and at X band.



FIG. 2. ESR spectrum obtained for oxygen-surplus sample 1 after 7.9-eV laser irradiation at 3 mJ/cm<sup>2</sup> per pulse and 50 Hz for 55 min at room temperature (RT). The "stick diagram" shows field splitting due to hyperfine interaction. The spectrum was recorded at 77 K and at X band.



FIG. 3. ESR spectra recorded for 7.9-eV laser-irradiated sample 1 (3 mJ/cm<sup>2</sup> per pulse, 50 Hz, 55 min., RT), (a) before and (b) after the KrF-excimer-laser (5.0 eV) irradiation at 20 mJ/cm<sup>2</sup> per pulse and 10 Hz for 15 min.

is found that the component B is a part of another fourline spectrum (referred to as spectrum B), as shown in Fig. 4. The spectrum B should be associated with hyperfine interaction with nuclei of  $I=\frac{3}{2}$ . The whole spectrum associated with the component C is still difficult to be resolved because of the overlap with the spectrum B.



FIG. 4. ESR spectra recorded for 7.9-eV laser-irradiated sample 1 (3 mJ/cm<sup>2</sup> per pulse, 50 Hz, 55 min, RT), after the subsequent 5.0-eV laser irradiation (20 mJ/cm<sup>2</sup> per pulse, 10 Hz, 15 min., RT). The "stick diagram" shows field splitting due to hyperfine interaction.

#### B. Models for the centers related to chlorine

As shown in Table I, chlorine is a possible impurity having nuclear spin of  $\frac{3}{2}$ , which is abundant in the sample. A pair of the four-line structures with an intensity ratio of 3 to 1 corresponds to the natural abundance ratio of the isotopes of chlorine ( ${}^{35}\text{Cl}{}^{37}\text{Cl}$ =75.77%:24.23%).<sup>12</sup> The ratio of the hyperfine splittings is the same as that of the magnetic moments of the two isotopes [ $\mu_N$ ( ${}^{35}\text{Cl}{})/\mu_N$ ( ${}^{37}\text{Cl}{}$ ) =1.20].<sup>12</sup> On the basis of these observations, it is concluded that defects responsible for spectra A and B are associated with chlorine.

Atomic chlorine is ruled out as a defect model responsible for either spectrum A or B. This is based on the following reasons: (i) the observed hyperfine splitting values of spectra A and B differ from that of atomic chlorine  $(A_{\parallel}/g\beta = 12.0 \text{ mT for } {}^{35}\text{Cl})$  and (ii) the present chlorinerelated radicals are stable at room temperature, while according to Griscom and Friebele<sup>9</sup> the atomic chlorine is only stable below 200 K. Based on the fact that the radical is observed in the oxygen-surplus silica, a possible candidate is a radical associated with excess oxygen. Shown in Fig. 5 is a comparison between two ESR spectra taken at two different positions in the same piece of sample 2. Both the components A and B are seen at the edge of the sample 2, which is oxygen surplus,<sup>13</sup> accompanied by a  $g_3 \approx 2.067$  peak of the peroxy radical. On the other hand, neither is observed at the center of the sample that is oxygen deficient.<sup>13</sup> It is, therefore, reasonable to assume that defect centers responsible for the spectra A and B are associated with both chlorine and oxygen.

Atkins, Symons, and co-workers<sup>14,15</sup> reported oxyradicals of chlorine in various matrices other than SiO<sub>2</sub>. The observed hyperfine splittings of  $\approx 11$  and  $\approx 9$  mT for spectrum *A*, and  $\approx 7$  and  $\approx 6$  mT for spectrum *B* are in agreement with those reported for the ClO<sub>3</sub> and ClO<sub>2</sub> radicals, respectively.



FIG. 5. ESR spectra obtained for 7.9-eV laser-irradiated sample 2 at two different sites  $(3 \text{ mJ/cm}^2 \text{ per pulse}, 50 \text{ Hz}, 10 \text{ min.}, \text{RT})$ : (a) center (oxygen deficient) and (b) edge (oxygen surplus). PR: peroxy radicals.

#### C. Computer simulation analysis

In order to extract accurate spin-Hamiltonian parameters, we performed simulations of the experimental ESR line shapes. The powder patterns were computed based on the resonance condition

$$H(m_I, \theta, \phi) = h v_0 / g \beta - (K / g \beta) m_I , \qquad (2a)$$

where

$$g^{2} = g_{1}^{2} \cos^{2}\theta + g_{2}^{2} \sin^{2}\theta \cos^{2}\phi + g_{3}^{2} \sin^{2}\theta \cos^{2}\phi ,$$
  

$$K^{2} = (A_{1}^{2}g_{1}^{2} \cos^{2}\theta + A_{2}^{2}g_{2}^{2} \sin^{2}\theta \cos^{2}\phi + A_{3}^{2}g_{3}^{2} \sin^{2}\theta \sin^{2}\phi)/g^{2} ,$$

*h* is the Planck constant,  $v_0$  the microwave resonance frequency,  $\beta$  the Bohr magneton, and  $m_I$  the nuclear spin quantum number (for  $I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ,  $-\frac{1}{2}$ ,  $\frac{1}{2}$ , and  $\frac{3}{2}$ ). The  $g_i$  and  $A_i$  (i = 1, 2, 3) are the principal values of the g and A tensors, respectively. The polar angles  $\theta$  and  $\phi$  define the direction of the applied field with respect to the principal axes of the g and A tensors. For the simulation of spectrum A, the inclusion of the second-order hyperfine term

$$H_{2nd} = -A_{\perp}^{2} (4g\beta h v_{0})^{-1} [(A_{\parallel}^{2} + K^{2})/K^{2}] [I(I+1) - m_{I}^{2}] -(2g\beta h v_{0})^{-1} [(A_{\parallel}^{2} - A_{\perp}^{2})/K]^{2} [g_{\parallel}g_{\perp}/g^{2}]^{2} \times \sin^{2}\theta \cos^{2}\theta m_{I}^{2},$$
(2b)

turned out to be critical, while a satisfactory fit was obtained for the spectrum *B* only with the first-order term in Eq. (2a). It should be noted that the  $H_{2nd}$  is an expression derived for the case of the axially symmetric powder pattern  $(g_{\parallel} = g_1, g_{\perp} = g_2 = g_3 \text{ and } A_{\parallel} = A_1, A_{\perp} = A_2 = A_3)$ .<sup>16</sup> Powder patterns are generated by calculating the resonance conditions for each of a large number of orientations corresponding to a uniform grid in  $\cos\theta$ - $\phi$  space and by histogramming on a magneticfield scale. The simulations for the spectra *A* and *B* are shown in Figs. 6(a) and 6(b), respectively. Here, the solid and the broken curves correspond to the observed and



FIG. 6. Computer simulated spectra for (a) the spectrum A attributed to ClO<sub>3</sub> and (b) the spectrum B attributed to ClO<sub>2</sub>. Solid and broken curves are experimental [after 7.9-eV laser irradiation (3 mJ/cm<sup>2</sup> per pulse, 50 Hz, 55 min., RT)] and simu-

the simulated ESR spectra, respectively. Table II gives the spin-Hamiltonian parameters employed in the simulations, together with those reported in other works.<sup>14,15</sup>

lated spectra, respectively.

As expected for radicals in glass, successful simulations

Species	g Matrix		A Matrix <sup>a</sup> (mT)							
	<b>g</b> <sub>1</sub>	<b>g</b> <sub>2</sub>	<b>g</b> <sub>3</sub>	$A_1/g_2\beta$	$A_2/g_2\beta$	$A_3/g_3\beta$	$\langle A_{\rm iso}/g\beta\rangle^0$	$\Delta A_{\rm iso}/g\beta^c$	$\Delta H_{p-p}^{a}$	Reference
a c	2.0070	2.0087	2.0087	15.0	11.1	11.1	12.4	0.5	0.3	Present study
	2.007	2.008	2.008	15.3	11.5	11.5	12.8			14, 15 °
CIO.	2.0030	2.0088	2.0180	6.85	-1.64	-2.06	1.05	0.5	0.5	Present study
	2.0036	2.0088	2.0183	7.3	-1.14	-1.54	1.54			14, 15 <sup>e</sup>

TABLE II. Spin-Hamiltonian parameters determined by computer simulation of experimental ESR line shapes (<sup>35</sup>Cl).

<sup>a</sup>Average values.

<sup>b</sup>Ensemble average of Gaussian distribution.

<sup>c</sup>Full width at half maximum of Gaussian distribution.

<sup>d</sup>Peak-to-peak derivative linewidth of the Lorentzian convolution function used in computing the spectra. <sup>e</sup>Single-crystal studies. for the spectra A and B were achieved only when statistical distributions were incorporated in the hyperfine coupling constants. We assume a Gaussian distribution for isotropic hyperfine coupling constant ( $A_{iso}$ ) and a fixed value for anisotropic hyperfine coupling constant ( $A_{aniso}$ ). In principle,  $A_{aniso}$  is also distributed. However, in the present case, the distribution in  $A_{aniso}$  is negligibly small in comparison with the magnetic-field resolution of the obtained ESR spectrum. The distribution was incorporated by computing a separate spectrum for 11 different values of  $A_{iso}$  and then summing them up according to the weighing factors given by the Gaussian distribution with a half width of  $\Delta A_{iso}$  (see Table II). Finally, they were convoluted with a Lorentzian linewidth function of  $\Delta H_{p-p}$  (peak-to-peak derivative width).

## D. Analysis of the ESR spectra

Since the sample is a glass, it is not possible to determine experimentally the correspondences between  $A_1$ ,  $A_2$ , and  $A_3$ , and  $A_{xx}$ ,  $A_{yy}$ , and  $A_{zz}$ , where x, y, and z are the principal axes of radicals. However, by symmetry consideration or by comparison with isoelectronic species, plausible correspondences can be obtained. Following the discussion given by Atkins, Symons, and coworkers<sup>14,15</sup> we decided the principal values of  $A_{aniso}$  tensor,  $B_{xx}$ ,  $B_{yy}$ , and  $B_{zz}$  (where  $A_{ii} = A_{iso} + B_{ii}$ , i = x, y and z) as shown in Table III. From the A values listed in Table III, we can then obtain information regarding the wave function of unpaired electron on chlorine. We assume that the wave function for unpaired electron on the ClO<sub>x</sub> radical is expressed as,

$$\Psi = C_{3s} |\mathrm{Cl}(3s)\rangle + C_{3p} |\mathrm{Cl}(3p)\rangle + C_{0} |\mathrm{other}\rangle , \qquad (3a)$$

where

$$C_{3s}^2 + C_{3p}^2 + C_0^2 = 1$$
 (3b)

The term  $|other\rangle$  takes into account the delocalization of unpaired electron over orbitals of ligand atoms, that is, 2p orbitals of oxygen atoms bound to the central chlorine. Fractional occupation of each orbital can be determined from the following relations:

TABLE III. Isotropic  $(A_{iso})$  and anisotropic hyperfine coupling constants  $(A_{aniso})$  determined for ClO<sub>3</sub> and ClO<sub>2</sub> (<sup>35</sup>Cl).

Hyperfine coupling constants (mT)					
Species	$\langle A_{\rm iso}/g\beta\rangle^{\rm a}$	$B_{xx}/g_{xx}\beta$	$B_{yy}/g_{yy}\beta$	$B_{zz}/g_{zz}\beta^{b}$	Reference
	12.4	-1.3	-1.3	2.6	Present study
ClO <sub>3</sub>	12.8	-1.3	-1.3	2.5	14,15
~ ~	1.05	5.80	-3.11	-2.69	Present study
CIO <sub>2</sub>	1.54	5.76	-3.08	-2.68	14.15

<sup>a</sup>Ensemble average of Gaussian distribution in  $A_{iso}$ .

bx, y, and z denote the principal directions of the radicals.

$$C_s^2 = A_{\rm iso} / A_s \tag{4a}$$

and

$$C_p^2 = A_{\rm aniso} / A_p \ . \tag{4b}$$

The values of 168.0 mT for  $A_s$  and 5.0 mT for  $A_p$  are taken.<sup>15</sup>

It is considered that ClO<sub>3</sub> radical has  $C_{3v}$  symmetry, as discussed by Atkins, Symons, and co-workers<sup>14,15</sup> The z axis is taken as the  $C_{3v}$  symmetry axis of the radical. From Eqs. (4a) and (4b), the  $A_{iso}$  of 12.4 mT and  $A_{aniso}$ of 1.3 mT determined for spectrum A give  $c_{3s}^2 = 0.074$ and  $C_{3p_2}^2 = 0.26$ , respectively. From Eq. (3b),  $C_0^2$  of 0.666 is obtained for three oxygens bound to chlorine. Thus, the localization is about 26% on the central Cl atom, while it is about 67% on the three ligand oxygens.

The  $C_{2v}$  symmetry is assumed for the ClO<sub>2</sub> radical.<sup>14,15</sup> We take the y axis parallel to the O-O direction, the z axis bisecting the O-Cl-O angle, and the x axis perpendicular to the plane which contains the y and z axes. Following the treatments made by Atkins, Symons, and coworkers<sup>14,15</sup> the anisotropic hyperfine tensor of spectrum B is further resolved into two axially symmetric tensors. The largest one is axially symmetric about the x axis and the other one about the z axis:

$$(5.80, -3.11, -2.69) = (5.94, -2.97, -2.97) + (-0.14, -0.14, 0.28) .$$
(5)

From the first component in the right-hand side of Eq. (5),  $A_{aniso}$  of 2.97 mT gives  $C_{3p_x}^2 = 0.582$ . This is in agreement with the expected  $b_1$  ground state of the ClO<sub>2</sub> radical.  $A_{aniso}$  of 0.14 mT from the second component gives  $C_{3p_z}^2 = 0.027$ .  $A_{iso}$  of 1.05 mT yields only a value of 0.006 for  $C_{3s}^2$ . It is considered that the slight s and  $3p_z$  characters may be accounted for by spin-polarization effect on the  $a_1$  molecular orbital, which has 3s and  $3p_z$  characters.<sup>14,15</sup> The  $C_0^2$  value of 0.385 is then obtained from Eq. (3b). Therefore, in the case of ClO<sub>2</sub> radicals, the unpaired electron mostly ( $\approx 58\%$ ) occupies the p orbital of chlorine and the rest ( $\approx 39\%$ ) occupies the p orbitals of two oxygens.

Fractional s-state density on the chlorine in the z direction is 0.07/(0.07+0.26)=0.21 for ClO<sub>3</sub> and 0.006/(0.006+0.03)=0.16 for ClO<sub>2</sub>. These values are suggestive of the orbital of  $sp^n$  type. Assuming Coulson's relationship between bond angle and hybridization ratio  $\lambda$  ( $\lambda = C_p/C_s$ ), the O-Cl-O bond angle  $\varphi$  can be calculated using

$$\varphi = \cos^{-1}[1.5/(2\lambda^2 + 3) - \frac{1}{2}]$$
 (6a)

and

$$\varphi = 2\cos^{-1}[\lambda^2 + 2]^{-1/2} \tag{6b}$$

for molecules with symmetry  $C_{3v}$  and  $C_{2v}$ , respectively. Calculated values of the O-Cl-O angle  $\varphi$  are 110° for ClO<sub>3</sub> and 134° for ClO<sub>2</sub>. Since the distribution in  $A_{iso}$  ( $\Delta A_{iso}$ ) can be interpreted by the variation in bond angle  $\varphi$ , the observed  $\Delta A_{iso}$  presumably reflects the interstitial site, where the ClO<sub>x</sub> radicals are located.

Molecular parameters obtained above are consistent with those reported in other works.<sup>14,15,17</sup> Thus we can conclude that the observed ESR spectra A and B are due to the ClO<sub>3</sub> and ClO<sub>2</sub> radicals, respectively.

# E. Formation mechanism of ClO<sub>x</sub> radicals

Spin concentrations were determined by double numerical integration of the first derivative spectra and comparison with a weak or strong pitch standard. Absolute spin density can be obtained within an error of  $\pm 50\%$ , while relative spin density between the same species within an error of  $\pm 10\%$ . Listed in Table IV are the spin concentrations of various species induced in the 7.9-eV laserirradiated sample 1.

Although the reaction path to the formation of  $ClO_x$  radical seems complicated, the net reaction is considered as follows:

$$Cl^0 + xO \rightarrow ClO_x$$
, (7)

where Cl<sup>0</sup> and x represent an atomic chlorine and a coordination number, respectively. First we discuss the origins of Cl<sup>0</sup> and O in the left-hand side of the Eq. (7). The states of excess oxygen in as-manufactured oxygensurplus silicas have been reported to be either in the form of peroxy linkage ( $\equiv$ Si-O-O-Si $\equiv$ ,  $\approx 10^{18}$  cm<sup>-3</sup>)<sup>18</sup>, or molecular oxygen ( $\approx 10^{17}$  cm<sup>-3</sup>).<sup>19</sup> It has been proposed that O<sub>2</sub> in silica dissociates into two atomic oxygens by photon irradiation with energies more than 5.1 eV;<sup>19</sup>

$$O_2 \rightarrow 2O$$
 . (8)

Griscom and Friebele proposed that  $Cl^0$  observed by ESR in x-irradiated low-OH silica deposited with the plasma method, arises from the scission of the  $\equiv$ Si-Cl bond:<sup>9</sup>

$$\equiv \mathrm{Si}\mathrm{-}\mathrm{Cl} \to \equiv \mathrm{Si}\mathrm{\cdot}\mathrm{+}\mathrm{Cl}^0 \ . \tag{9}$$

Since the oxygen-surplus sample 1 exhibits neither the 5.0-eV nor the 7.6-eV absorption band<sup>18</sup> associated with oxygen vacancies ( $\equiv$ Si-Si $\equiv$ ),<sup>20</sup> it is considered that the sample 1 contains no oxygen vacancies as a precursor of the E' center. Therefore, it is likely that the reaction of Eq. (9) is dominant in the formation of the E' centers. If all the Cl<sup>0</sup>'s produced through the reaction of Eq. (9) react with oxygens to form ClO<sub>x</sub> radicals, the concentration of the E' center is expected to be equal to that of the

TABLE IV. Spin concentrations of paramagnetic defect centers in the low-OH oxygen-surplus silica (sample 1) irradiated with a 7.9-eV laser ( $\approx 3 \text{ mJ/cm}^2$  per pulse, 50 Hz, 55 min.).

Species	Spin density $(cm^{-3})$
E' center	$1.0 \times 10^{16}$
Peroxy radical (PR)	$3.7 \times 10^{17}$
ClO <sub>2</sub>	$4.8 \times 10^{16}$
ClO <sub>3</sub>	1.8×10 <sup>16</sup>

 $\text{ClO}_x$  radicals. However, it is clear from Table IV that the concentration of the E' centers falls short of that of the  $\text{ClO}_x$  radicals by a factor of 7. One way to explain the discrepancy is to assume that the E' centers initially created by 7.9-eV laser irradiation through the reaction of Eq. (9) were transformed into other species. Since sample 1 presumably contains molecular oxygen,<sup>18</sup> it is considered that the E' centers react with molecular oxygens dissolved in the glass. It has been demonstrated that the E' center can react with molecular oxygen to form peroxy radical (PR):<sup>21,22</sup>

$$\equiv \mathbf{Si} \cdot + \mathbf{O}_2 \rightarrow \equiv \mathbf{Si} \cdot \mathbf{O} \cdot \mathbf{O} \cdot . \tag{10}$$

An analogous reaction of the E' center with atomic oxygen may be also involved under the assumption that the reaction of Eq. (8) occurs:

$$\equiv \mathrm{Si} \cdot + 2\mathrm{O} \to \equiv \mathrm{Si} \cdot \mathrm{O} \cdot \mathrm{O} \cdot . \tag{11}$$

The reaction of Eq. (10) is reported to be a thermallyactivated process observed at more than 200 °C,<sup>21,22</sup> since the process is a diffusion-limited reaction of O<sub>2</sub> which is mobile in the network above 200 °C. Thus, at room temperature the reaction of Eq. (11) seems to be more dominant than the reaction of Eq. (10). The above assumption on the basis of Eqs. (9)-(11),  $[Cl^0]=[E']_{init}$  and  $[E']_{init}=[E']+[PR]$ , is consistent with the fact that  $[ClO_x]=6.6 \times 10^{16} < 3.8 \times 10^{17}=[E']+[PR]$ .

An isochronal annealing experiment was performed on sample 1 immediately after the 7.9-eV laser irradiation ( $\approx 3 \text{ mJ/cm}^2$  per pulse, at 50 Hz, for 10 min.). Because of the interference of each ESR component, the amplitudes of the major components were plotted in Fig. 7 rather than obtaining their absolute spin densities. It is clear in Fig. 7 that the growth of the ClO<sub>3</sub> (A) and ClO<sub>2</sub> (B) radicals is observed at 100 and 200 °C. At 300 °C, the



FIG. 7. Isochronal annealing curves for the components A (ClO<sub>3</sub>), B (ClO<sub>2</sub>), C, the peroxy radical (PR), and the E' center observed in oxygen-surplus sample 1 induced by 7.9-eV laser irradiation (3 mJ/cm<sup>2</sup> per pulse, 50 Hz, 10 min., RT). All data were taken at 77 K and X band with a microwave power of 1  $\mu$ W for the E' center and 5 mW for the other species.

ClO<sub>2</sub> radicals still grow up to 3-4 times of the initial concentration, while the ClO<sub>3</sub> radicals disappear. Considering only the shapes of the annealing curves, the anticorrelation between the ClO<sub>2</sub> and the ClO<sub>3</sub> suggests the conversion from the ClO<sub>3</sub> to the ClO<sub>2</sub> upon heat treatment above 300 °C. Of course, other reactions might be also involved,<sup>17</sup> since both the ClO<sub>2</sub> and ClO<sub>3</sub> radicals increase at 100 and 200 °C. At present, our ESR and isochronal annealing data are not sufficient to propose any models for the reaction. Further investigation is necessary to clarify this.

It is interesting to compare the present ESR spectra with those obtained in the same type of silica irradiated with different photon energies. Although not well resolved in the spectra of silica irradiated with a 6.4-eV excimer laser,<sup>23</sup> a trace of ClO<sub>2</sub> radicals at  $g \approx 2.025$ , which corresponds to the component B, can be recognized with much weaker amplitude. The difference in the amplitude of the ClO<sub>2</sub> radical may be accounted for by the photon-energy dependence of absorption coefficients of  $\equiv$  Si-Cl and O<sub>2</sub>, and the quantum yields of the reactions (8) and (9). For example, the absorption coefficient of the oxygen molecule at 157 nm (7.9 eV) is about four orders of magnitude larger than that at 193 nm (6.4 eV).<sup>24</sup> A similar isochronal annealing behavior of ClO<sub>2</sub> can be also observed in ESR spectra of the 6.4-eV laserirradiated silica.

#### IV. SUMMARY

An ESR study was made on a series of high-purity silica glasses exposed to vuv (7.9-eV) excimer laser. We ob-

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served defect centers, which are stable at room temperature, in a type of high-purity silica glass (low-OH, oxygen surplus). The ESR spectrum comprises a pair of four-line structures, both due to hyperfine interaction with a single chlorine nucleus of  $I = \frac{3}{2}$ . They are identified as  $ClO_x$ (x=2,3) radicals on the basis of spin-Hamiltonian parameters determined by computer simulation analysis. The generation of  $ClO_x$  radicals is considered to be the reaction between atomic chlorine and oxygen, which are respectively produced by photodecomposition of chlorine impurities and molecular oxygen existing abundantly in the sample. The  $ClO_x$  radicals show peculiar behavior during thermal treatment, where the kinetics of oxygen and chlorine are suggested to be involved. The present investigation demonstrates that these radicals can be probes to study the reaction kinetics of chlorine and oxygen, which are of importance for the development of silica glass resistant to intense uv and vuv irradiation.

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