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Triplet-state defect in high-purity silica glass

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Electron-spin resonance in the spectral region about $g=4$, believed to be due to a triplet state, is investigated in γ-irradiated high-purity silica glasses. The triplet defect is found only in oxygen-deficient samples. The results of γ-irradiation combined with hydrogen treatment suggest the pivotal role of the oxygen vacancy in the formation mechanism of the triplet defect.

Amorphous silicon dioxide is a material that finds applications in many of the fields upon which modern optoelectronics is based, for instance, as the core of low-loss optical waveguides and as the gate oxide in silicon-based metal-oxide semiconductor devices. For this reason, considerable current interest centers on the influences of nuclear and space radiation on the optical and electronic properties of this material. Recently, Griscom[1] reported a triplet-state defect in γ-irradiated silica, detected by electron-spin resonance (ESR). Detailed experimental results were presented and models were proposed for this defect, as well as a delocalized E' center (referred to as the $E'\delta$ center). The defects were found in silica containing a substantial amount of chlorine impurities, and thus the defects were assigned to variations of a chlorine-ion-decorated "SiO_4" vacancy, as shown in Fig. 1. The E' center normally observed (referred to as $E'\gamma$ center) is also shown in Fig. 1 for comparison.

The present paper reports several new features of both the triplet and the $E'\delta$ center. Specifically, it is found that (i) oxygen vacancies, in addition to chlorine impurities, must be present for the defects to be induced, (ii) fluorine impurities can also give rise to these defects, and (iii) the termination of oxygen vacancies by hydrogen diffusion results in the suppression of these defects.

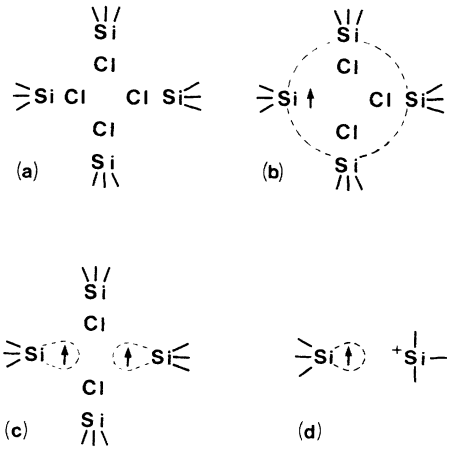

FIG. 1. Proposed models for defect structures in Cl-containing a-SiO_2: (a) chlorine configuration in unirradiated glass; (b) $E'\delta$ center; (c) triplet; (d) $E'\gamma$ center (after Ref. 1).

The samples used in the experiments are shown in Table I. The chlorine contents of the samples were obtained by radioactivation analysis. The hydroxyl content was obtained from the IR absorption[2] at 3600 cm^{-1}. The presence of fluorine was detected by the Raman spectrum[3] at 930 cm^{-1} measured in the backscattering mode, using an Ar-ion laser source (514.5 nm, 200 mW). The samples for the optical-absorption measurements were 40-mm-long rods with a diameter of 10 or 15 mm. Samples for the ESR measurements were two 25×2-mm^2 strips cut from a glass plate 40 mm in diameter and 1.0 mm thick. The ESR measurements were performed at liquid-nitrogen temperature using a JEOL RE-2XG operating at X-band frequency. Optical absorption in the ultraviolet region was measured using a Shimadzu UV-160. γ irradiation was performed at room temperature (RT) with a ^{60}Co source at dose rates of 120 Gy/h to a total of 20 kGy. Hydrogen treatments were performed either at room temperature (3 atm, 1 week), or at 500 °C (3.8 atm, 12 h). After the hydrogen treatment at 500 °C, the samples were kept at 90 °C for 15 h to remove remaining hydrogen molecules.

Figure 2 shows the ESR signal detected in γ-irradiated sample 2. The signal in the spectral region of about $g=4$ [1620 G, Fig. 2(b)], is assumed to correspond with the signal observed by Griscom[1] at the same region, and will be referred to as the "triplet" defect. Figure 3 shows the intensity of the triplet observed in various γ-irradiated samples, as a function of the chlorine content of that sample. The figure shows that there are samples which contain chlorine but do not exhibit the triplet, such as samples 6–8. Furthermore, the triplet can be induced in sample 5, which contains no chlorine but instead contains fluorine impurities. The result suggests that the existence of

TABLE I. Sample list, where D represents detected and ND below the detection limit.

Sample[a]	Manufacturing method	Impurity (ppm) Cl	F	OH	5.0-eV absorption (OD/cm)	γ-ray induced defects (ESR) $E'\gamma$	$E'\delta$	Triplet
1 (SA1)	Ar plasma	12000	ND	ND	0.170	D	D	D
2 (SA2)	Ar plasma	3200	ND	0.8	0.110	D	D	D
3 (SA3)	Ar plasma	1000	ND	3.0	0.070	D	D	D
4 (SPN)	Ar plasma	1600	ND	20	0.014	D	D	D
5 (SFF)	soot	ND	2000	ND	0.008	D	D	D
6 (WN7)	soot	4700	ND	ND	ND	D	ND	ND
7 (OH2)	Ar plasma	690	ND	300	ND	D	ND	ND
8 (P3F)	Ar+O_2 plasma	370	ND	0.5	ND	D	ND	ND
9 (DF8)	direct	ND	ND	1000	ND	D	ND	ND

[a]Sample names in parentheses are the names used in Ref. 4.

chlorines is not sufficient to give rise to the triplet. The common denominator of the samples in which the triplet is detected is the observation of the 5.0-eV ($B_2\alpha$) absorption band prior to irradiation (Table I). Accepting our previous assignment[4] of the 5.0-eV bands to oxygen vacancies (≡Si−Si≡), the triplet is detected only in oxygen-deficient samples. Limited to the oxygen-deficient samples, a good relation between the triplet intensity and impurity (chlorine or fluorine) content can be seen in Fig. 3.

Another common characteristic of the oxygen-deficient glass is the growth of the $E'\delta$ center. The spectra of the $E'\delta$ center induced by γ irradiation in sample 2 is shown in Fig. 3(a). As shown in Table I, the $E'\delta$ center is observed in the same samples in which the triplet is present, indicating that the two defects share something in common. The $E'\gamma$ center, on the other hand, was observed in all samples examined.

Table II shows the effect of hydrogen treatment, performed at room temperature and 500 °C prior to γ irradiation, on the triplet and $E'\delta$ center intensities. The effect on the triplet is similar to that on the $E'\delta$ center, but is different from that on the $E'\gamma$ center. The hydrogen treatment at 500 °C results in a considerable decrease of the $E'\delta$ center and completely suppresses the triplet. The hydrogen treatment at room temperature resulted only in a slight increase of both the triplet and $E'\delta$ center. On the other hand, hydrogen treatment greatly increases the $E'\gamma$ center, regardless of whether the treatment was performed at room or high temperature.

Hydrogen treatment at 500 °C terminates the oxygen vacancy (5.0-eV band) as shown in Fig. 4. The termination is believed to occur in the following manner:

$$\equiv Si-Si\equiv + H_2 + 500\,^{\circ}C \rightarrow \equiv Si-H\ H-Si\equiv . \quad (1)$$

Reaction (1) does not occur when the hydrogen treatment is performed at room temperature, because the 5.0-eV band does not decrease. This termination of oxygen vacancy, and not hydrogen itself, seems to play the central role in suppressing the triplet and $E'\delta$ center. The reason is that the hydrogen molecules remaining in the glass after hydrogen treatment at 500 °C were removed by keeping the samples at 90 °C before γ irradiation, and that hydrogen treatment at room temperature does not affect the oxygen vacancy, the triplet, or the $E'\delta$ center. (This hydro-

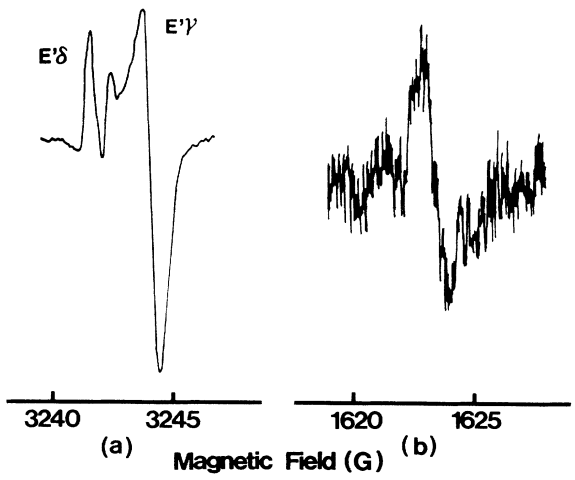

FIG. 2. ESR signal induced in γ-irradiated sample 2: (a) spectral region of $g=2$; (b) spectral region of $g=4$.

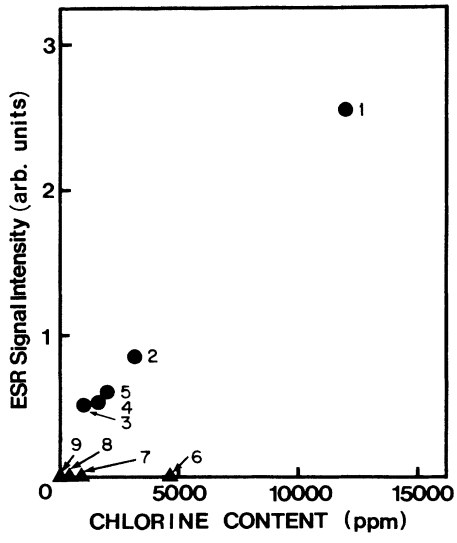

FIG. 3. ESR signal intensity of the triplet as a function of chlorine content. Note the impurity content of sample 5 is fluorine.

TABLE II. Effect of hydrogen treatment on various defects.

Treatment	ESR signal intensity (normalized) $E'\gamma$	$E'\delta$	Triplet
γ only	1.00	1.00	1.00
RT $H_2+\gamma$	1.69	1.07	1.06
500 °C $H_2+\gamma$	1.65	0.43	0.00

gen diffused into the glass at room temperature is confirmed by the increase of the $E'\gamma$ center by hydrogen treatment at room temperature, as shown in Table II).

In order to interpret the experimental data described above within the context of Griscom's model,[1] it is necessary to make several assumptions. First, since the triplet and $E'\delta$ centers are induced in sample 5, which contain no chlorine but instead contain fluorine impurities, it would have to be assumed that fluorine impurities are incorporated in the glass in the same manner as the chlorine impurities. This would mean SiO_4 tetrahedral vacancies decorated by fluorines. Second, no detectable difference in the ESR spectra of the triplet and $E'\delta$ centers was observed between the chlorine-containing samples and fluorine-containing sample; therefore, the impurities existing next to the triplet or the $E'\delta$ center, regardless of whether it is chlorine or fluorine, must not have any effect on the ESR spectrum. Third, it must be assumed that there are multiple manners in which the chlorine is incorporated in the SiO_2 network, since neither the triplet nor the $E'\delta$ center could be observed in the sample 6, which contains substantial chlorine (4700 ppm); therefore the chlorine would have to exist in a form other than the SiO_4 tetrahedral vacancy in this sample.

An alternative to the third assumption is that the chlorine-decorated tetrahedral vacancy exists in sample 6, but the lack of oxygen vacancies prevents the formation of the triplet and $E'\delta$ center. As described above, the common denominator of all samples in which the triplet and $E'\delta$ centers are induced is the observation of the 5.0-eV absorption band prior to irradiation. Elimination of the oxygen vacancy, whether during the manufacturing process or by the hydrogen treatment, results in the suppression of the triplet and $E'\delta$ centers, suggesting the pivotal role of oxygen vacancy in the formation mechanism of the two centers.

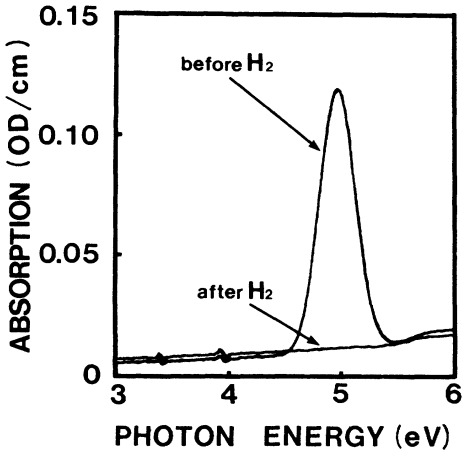

FIG. 4. Optical absorption of sample 2 before and after hydrogen treatment at 500 °C.

If, on the other hand, it is assumed that the triplet and $E'\delta$ centers are induced independent of impurities, the experimental results suggest they are related to oxygen vacancies. This would require a slight revision of Griscom's model, namely, that instead of the SiO_4 tetrahedral vacancy, the centers are formed at the site of a simple oxygen vacancy. The triplet in this scheme would be a biradical oxygen vacancy, in other words, two E' centers ($\equiv Si\cdot\ \cdot Si\equiv$) with the electrons having the same spin direction. The $E'\delta$ center would be an unpaired spin delocalized over the two neighboring silicons.

Whether a direct or indirect precursor, the oxygen vacancy is suggested to be a requirement for the growth of these centers. The assignment of its exact role in the formation mechanism of these centers is essential, but must wait the results of the continuing research.

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