Photoluminescence of oxygen-deficient-type defects in γ-irradiated silica glass

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Abstract

We studied the photoluminescence (PL) band in high-purity oxygen-deficient-type silicas both before and after high-dose γ-irradiation. With a high γ-irradiation dose of up to 10 MGy, a new PL band was induced at 3.9 eV and observed under excitation by 4.66 eV photons, along with the previously observed 2.25, 2.7 and 4.3 eV PL bands. Among the samples we investigated, this PL band was found only in high-dose γ-irradiated oxygen-deficient-type silica glass with the highest oxygen-deficient-associated defect structures [oxygen vacancy, E′ center and E0 center]. These results indicate the possibility that this PL band is associated with an extreme oxygen-deficient-associated defect structure, at present unknown, in the silica glass which was introduced during the manufacturing process and which is enhanced by γ-irradiation.

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1. Introduction

Optical absorption, photoluminescence (PL), electron spin resonance (ESR), and other methods have been used to study the structural defects in silica glass [1]. The PL originating from the oxygen vacancy (O3 ≡ Si–Si≡O3) [2–6] and the non-bridging oxygen hole center (NBOHC, O3 ≡ Si–O], where ⊳ represents an unpaired electron) [7–13] has been studied in depth using the peak energy, full width at half maximum (FWHM) and decay time (τ).

Our previous works [14–20] describe the seven PL bands at 1.8 eV (FWHM: ~0.4 eV, τ: ~200 ns) [15–17], 2.1 eV (FWHM: ~0.32 eV, τ: unknown) [20], 2.15 eV (FWHM: ~0.5 eV, τ: ~150 ns) [20], 2.25 eV (FWHM: ~0.4 eV, τ: ~25 ns) [14], 2.7 eV (FWHM: ~0.4 eV, τ: ~10 ms) [14], 3.15 eV (FWHM: ~0.4 eV, τ: ~10 μs) [18] and 4.3 eV (FWHM: ~0.4 eV, τ: ~few ns) [14] in as-grown and high-dose (10 MGy) γ-irradiated (60Co) high-purity oxygen-deficient silica glass (excited by visible and ultraviolet light).

There is a strong consensus in the literature that PL in the 4.2–4.4 eV range arises from oxygen vacancy centers [3]. Generally, the 2.7 eV and 4.3 eV PL intensities are strong in the oxygen-deficiency-type samples, and they are always observed together. Therefore, our conclusion is that the origin of the two PL bands is identical, i.e., the two PL bands are transitions from the excited state to the ground state of the oxygen vacancy. On the other hand, there is a report that the origin of the two PL bands is not identical. Tohmon et al. [4,5] have shown the relationship between 2.7 and 4.4 eV PL bands and oxygen vacancy by an ab initio molecular-orbital calculation using the cluster (HO)3Si–Si(OH)3. Though verification of the existence of the 4.4 eV PL band failed, the existence of the 2.7 eV PL band and the two absorption bands was verified [4,5]. Itoh et al. [21] conclude that the 2.7 eV PL band was the recombination of the self-trapped excitation. In our previous work [22], we measured the PL band of various thermally heat treated silica glasses. In the ‘after the
heat treatment' sample, we did not observe the 4.3 eV PL band, though we did observe the 2.7 eV PL band. From these results, we suggest that there is no common origin of these two PL bands. It is important to understand the emission mechanisms of these two PL bands. If the emission mechanism is to be understood, it seems to us that we first need to understand the characteristics of the PL under various conditions. Continuing our previous work, we investigated the PL properties of various types of silica’s before and after high-dose γ-irradiation (dose: 10 MGy).

The purpose of this paper is to present the results of a detailed investigation of the new PL band observed in oxygen-deficient-type silica before and after high-dose γ-irradiation. We also report our recent observation of a PL band in various types of silicas before and after high-dose γ-irradiation.

2. Samples

The samples used for experiments are listed in Table 1. They are divided into six groups depending on the synthesis process. The upper three groups are synthesized with three different plasma methods by two different manufacturers, the group four with flame hydrolysis, and the group five with CVD soot remelting. All the samples belonging to the above groups are high-purity amorphous silica (i.e., silica glasses). The difference among the samples in the group one (A1–A4) or that of the samples in group two (B1 and B3) is the oxygen amount during the synthesis. Depending on the synthesis process and the oxygen amount therein, silica glasses are classified into (mainly) four categories:

<table>
<thead>
<tr>
<th>Group</th>
<th>Sample name</th>
<th>Category</th>
<th>Manufacturing method</th>
<th>Impurity (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A1</td>
<td>Oxygen-deficient PO₂ = 1.0%</td>
<td>Ar plasma</td>
<td>12000 0.6</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>Oxygen-deficient PO₂ = 1.5%</td>
<td>Ar plasma</td>
<td>3200 0.8</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>Oxygen-deficient PO₂ = 5.0%</td>
<td>Ar plasma</td>
<td>1000 3.0</td>
</tr>
<tr>
<td></td>
<td>A4</td>
<td>Oxygen-deficient PO₂ = 15.0%</td>
<td>Ar plasma</td>
<td>400 3.3</td>
</tr>
<tr>
<td>2</td>
<td>B1</td>
<td>Oxygen-deficient 1.15:1</td>
<td>O₂ plasma</td>
<td>1200 3.0</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>Oxygen-deficient 1:1</td>
<td>O₂ plasma</td>
<td>340 3.0</td>
</tr>
<tr>
<td>3</td>
<td>P</td>
<td>Oxygen surplus</td>
<td>Ar + O₂ plasma</td>
<td>370 0.6</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>High-OH</td>
<td>Flame hydrolysis</td>
<td>ND 1000</td>
</tr>
<tr>
<td></td>
<td>S1</td>
<td>Unknown (B₂β)</td>
<td>CVD soot remelting</td>
<td>0.3 200</td>
</tr>
<tr>
<td>5</td>
<td>S2</td>
<td>Oxygen-deficient</td>
<td>CVD soot remelting</td>
<td>0.2 ND</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>Oxygen-deficient</td>
<td>CVD soot remelting</td>
<td>0.3 ND</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>Oxygen-deficient</td>
<td>CVD soot remelting</td>
<td>ND 6.0</td>
</tr>
</tbody>
</table>

PO₂: oxygen partial pressure during the synthesis.
CVD: chemical vapor deposition.
ND: not detected.

3. Experiment

Optical absorption and luminescence were studied for samples with cubic shape (20 × 20 × 20 mm³), or right cylindrical shape with a diameter 10 mm and a height 10 mm. All the sample surfaces including the side periphery were mirror polished. The absorption spectra in the visible-ultraviolet region were obtained with a Shimadzu UV-160A double-beam spectrometer.

PL measurements were made with a monochromator (Jobin-Yvon, HR250) equipped with a multichannel detector (Atago Max-3000). The PL excitations were produced by illuminating the samples with an Nd:YAG laser at 266 nm (4.66 eV). Time-resolved PL spectra were measured with a pulse generator (Stanford Research System, DG535)
which determines the delay time \((td)\) after a pulsed excitation and exposure time \((tc)\). Generally, \(td = 0\) s is when the light emission begins. However, it was difficult to accurately determine the time when light emission started with the measuring instruments used in this experiment. High precision measuring instruments are necessary in order to accurately determine when light emission starts. In this experiment we standardized the value of \(td\) as the time between when the sample was exposed to the exciting light and the start of spectroscopy. This can be controlled by the output waveform of the pulse generator and timing of the observation of the spectrum. First, various adjustments were carried out, while the exciting light and output waveform of the pulse generator were observed with the digital oscilloscope. In this way it was possible to adjust the timing. Next, measurement of the spectrum of the exciting light was carried out, while \(td\) was adjusted. The result of this work was that we were able to determine the \((\sim 20\) ns) error in the response time of the gate circuit of the multichannel detector. It was difficult to remove the effect of this error. In the spectroscopy of PL bands with emission lifetimes over 100 ns, the effect of this error can be disregarded. However, the effect of this error cannot be disregarded in the spectroscopy of PL bands with emission lifetimes of 10 ns or less. Therefore, the measurements were carried out, when \(td\) was observed in ns order. The PL decay was measured by observing the decay of the PL after a pulsed excitation with the Nd:YAG laser. The voltage across a resistor \((R = 50 \Omega - 1 \Omega)\) carrying the output current from a photomultiplier (Hamamatsu, E2762) was recorded with a digital oscilloscope (Tektronix, 2440). The PL spectra were corrected for the non-ideal response of the detection system. Measurements were carried out between 290 and 20 K.

Electron spin resonance (ESR) spectra were obtained by a JEOL JES-RE2X spectrometer for a group of samples cut into shapes of 1.5 \(\times\) 2.0 \(\times\) \((8–20)\ mm^3\) at 77 K. The microwave frequency was in the X band (near 9.4 GHz), with a power of 1 \(\mu\)W \((\sim 1\) mW) for \(E\) centers \((^{29}\text{Si}\ \text{hf structure})\), and 5 mW for NBOHC and peroxy radicals (PRs, \(\text{O}_3\Sigma\text{Si-O-O})\). The \(\gamma\)-irradiation was from a \(60\text{Co}\) source with a dose rate of 10 kGy/h to achieve total doses of 10 MGy at room temperature in air. The relative error in intensity of PL was within \(\pm 5\%\) using this irradiation method.

4. Results

Fig. 1 shows the spectra of \(\gamma\)-irradiated sample A1 (oxygen-deficient-type) excited at 4.66 eV with the Nd:YAG laser and for various \(td\) \((tc = 200\) ns\) at 290 K. Fig. 2 shows the spectra of (a) \(td < 10\) ns and (b) \(td = 40\) ns of Fig. 1. As shown in Fig. 2(a), this PL spectrum contains two PL bands including a 4.3 eV PL band. The 4.3 eV PL band \((\tau: \sim\text{few ns})\) originates from oxygen vacancy centers \((\text{O}_3\Sigma\text{Si-Si}=\text{O}_3)\) [23,3]. Fitting the data to two Gaussian curves gives a peak energy, \(Ep\), of 3.88 eV and a FWHM of 0.4 eV for the 3.9 eV PL band (curve 1), and an \(Ep\) of 4.32 eV and a FWHM of 0.4 eV for the 4.3 eV PL band (curve 2) (see Fig. 2(b)). It is difficult to estimate the decay time of the 3.9 eV PL band because the PL intensity is very weak and overlaps the exciting light (4.66 eV). Among the samples we investigated, the 3.9 eV PL band was found only in \(\gamma\)-irradiated sample A1.

Fig. 3 shows the temperature dependence of the 3.9 eV PL intensity for \(\gamma\)-irradiated sample A1 over 20–290 K. These PL intensities were normalized to the intensity at room temperature. The PL intensity decreases with increasing temperature. This decrement in the PL intensity is due to temperature quenching, i.e., the PL intensity decreases with increasing non-radiative decay.

Table 2 shows the PL bands (2.25, 2.7, 3.9 and 4.3 eV) for all samples before and after \(\gamma\)-irradiation of 10 MGy. As shown in Fig. 4, the 2.25, 2.7 and 4.3 eV PL intensities decreased with increasing \(PO_3\). Fig. 5(a) and (b) show optical absorption spectra of four typical samples, the oxygen-deficient A1, oxygen surplus P, high-OH D and \(B_2/\beta\) S1, before and after the \(\gamma\)-irradiation of 10 MGy, respectively. The unirradiated A1, P and S1 samples have their characteristic absorption bands, namely, the 5.0 eV band (oxygen vacancy) [4], the 3.8 eV band (peroxy linkage) [23,24], and the 5.15 eV band (\(B_2/\beta\)) [4], respectively. Note that the peak around 5.8 eV that appeared in the unirradiated A1 is not due to an \(E_0\) center since \(E\) centers have not been detected in all the unirradiated samples including A1 [23].

The absorption is significantly increased by irradiation in all the four types of samples, especially in the high energy region of 4–6 eV. Similar irradiation dependence is seen for samples A1–A4 (see Fig. 6). Since the two main causes of the absorption bands in this energy region are the oxygen vacancy (5.0 eV) [4,25], and the \(E\) center (5.8 eV) [26], the amounts of these two defects were examined. First, the amount of radiation-induced \(E\) centers was
examined by ESR. As seen in Fig. 7, E’ centers were observed in all samples, and the intensity is very large in A1, A2, and D. Therefore, the large absorption increase in irradiated A1, A2, and D samples appears to be due to the E’ centers.

The wide-range scan and narrow-range scan ESR spectra of the 10 MGy-γ-irradiated Sample A1 are shown in Fig. 8(a) and (b), respectively. These spectra, which were measured at 1 mW, contained eight sets of doublets, which are labeled 1–8, excluding the intense resonance in the central region. The separation of the doublets was 40.9 mT for doublet 1, 9.5 mT for doublet 2, 7.6 mT for doublet 3, 4.26 mT for doublet 4, 3.0 mT for doublet 5, 2.5 mT for doublet 6, 1.6 mT for doublet 7 and 1.06 mT for doublet 8. Each doublet is thought to be due to an hf interaction with the 29Si isotope, (which has an abundance of 4.7% in nature) and has a nuclear spin of I = 1/2. These ESR signals appeared in the ESR spectra of all samples that were subjected to γ-irradiation. As shown in Fig. 8(a), the position of the (middle) magnetic field of doublet 1 is shifted slightly towards a lower magnetic field with respect to the position of the central line (E’ center). This shift has been reported by Griscom et al. [27] and Jani et al. [28]. The cause of this shift is not completely clear though we suspect it is connected with the hyperfine structure. However, we cannot eliminate the possibility of other, as yet unknown, influences.

Fig. 9 shows the change in amplitude of doublets 1, 4, 5 and 8 with microwave power. All of the curves of doublet intensity versus microwave power are similar. On the basis of these results, we assume that the observed doublets are due to the primary 29Si hf structure of the E’ center.

Fig. 10 shows the intensity of the doublets 1 (open square), 7 (closed circle), and 8 (open triangle) as a function of oxygen partial pressure PO2 during the plasma CVD process for samples A1–A4. These samples were used to investigate the effect of oxygen in silica glass because they were synthesized under different oxygen pressures. With these samples we were able to study the effect of oxygen by measuring the intensity of the doublet as a function of PO2. The doublet intensity decreased with increasing PO2. This suggests that the doublet is due to the oxygen-deficient structure.

### 5. Discussion

First, we discuss the results for the 3.9 eV PL band. As shown in Fig. 2(a), this PL spectrum contains two PL bands including a 4.3 eV PL band. The 4.3 eV PL band (τ: ~few ns) originates from oxygen vacancy centers (O3Si−Si=O3) [2,3]. Fitting the data to two Gaussian curves gives a peak energy, Ep, of 3.88 eV and a FWHM of 0.4 eV for the 3.9 eV PL band (curve 1) and an Ep of 4.32 eV and a FWHM of 0.4 eV for the 4.3 eV PL band (curve 2) (see Fig. 2(b)). It is difficult to estimate the decay time of this PL band because the PL intensity is very weak and overlaps the 4.3 eV PL band. From the result of PL
spectrum change for the change of Td, we can estimate that the PL lifetime is of ns order (see Fig. 1). As shown in Fig. 3, the PL intensity decreases with increasing temperature. This decrement in the PL intensity is due to temperature quenching, i.e., the PL intensity decreases with increasing non-radiative decay. As shown in Table 2, this PL band was found only in high-dose \( \gamma \)-irradiated oxygen-deficient-type sample A1. These results suggest that the 3.9 eV PL band is associated with an extreme oxygen-deficient-associated defect structure in the silica glass which was introduced during the manufacturing process and which is enhanced by \( \gamma \)-irradiation.

Next, we discuss the formation of the various defects in sample A1 by \( \gamma \)-irradiation. Sample A1, which was manufactured by the Ar plasma method in the presence of a very small amount of oxygen \( P_{O_2} = 1.0\% \), contained the highest concentration of oxygen vacancies and \( E' \) centers (see Figs. 6 and 7). On the other hand, from the wide-range scan and narrow-range scan ESR spectra observation, we obtained an ESR signal associated with oxygen-deficient-associated defect centers [Si clusters or SiO\(_x\) (\( x < 2 \)) structure] in the \( \gamma \)-irradiated sample A1 (see Fig. 8(b)). Doublets 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>PL Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.25 eV</td>
</tr>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>A1</td>
<td>X</td>
</tr>
<tr>
<td>A2</td>
<td>X</td>
</tr>
<tr>
<td>A3</td>
<td>X</td>
</tr>
<tr>
<td>A4</td>
<td>X</td>
</tr>
<tr>
<td>B1</td>
<td>X</td>
</tr>
<tr>
<td>B3</td>
<td>X</td>
</tr>
<tr>
<td>P</td>
<td>X</td>
</tr>
<tr>
<td>D</td>
<td>X</td>
</tr>
<tr>
<td>S1</td>
<td>X</td>
</tr>
<tr>
<td>S2</td>
<td>X</td>
</tr>
<tr>
<td>S3</td>
<td>X</td>
</tr>
<tr>
<td>S4</td>
<td>X</td>
</tr>
</tbody>
</table>

O: detected.
X: not detected.

Fig. 4. Relationship between the partial oxygen pressure and the PL intensity of 2.25, 2.7, and 4.3 eV of \( \gamma \)-irradiated samples A1–A4.

Fig. 5. Optical absorption spectra of four different types of silicas [A1: oxygen-deficient (B2α), P: oxygen surplus, D: high-OH, S1: oxygen-deficient (B2β)]: (a) before, (b) about three months after \( \gamma \)-irradiation.

(9.5 mT), 5 (3.0 mT) and 6 (2.5 mT) in the ESR spectra of the \( \gamma \)-irradiated silica glass samples are similar to the primary hf (7 ± 2 mT) and superhyperfine (2.7 mT) structures.
of a dangling $^{29}$Si atom backbonded to three Si atoms, where the $7 \pm 2$ mT structure represents the D center in amorphous silicon [29]. The hf splitting decreases from 40 mT to 7–11 mT when moving from an $E_0$ center to a $P$ or D center [30]. Doublets 3 (7.6 mT) and 8 (1.06 mT) have similar hf (7.4 and 1.04 mT) structures to those observed in hydrogen-associated defect centers in a-$SiO_2$:OH [31]. The signals for doublets 3 and 8 were stronger in the ESR spectrum of the $\gamma$-irradiated oxygen-deficient, OH-free-type silica (A1) than in the ESR spectra of the other $\gamma$-irradiated samples. On the basis of these results, we conclude that the observed hf (7.4 and 1.04 mT) structures in the ESR spectrum of a-$SiO_2$ are not due to hydrogen-associated defect centers.

From these results, it is clear that the various defects in which the oxygen-deficient structure is involved were formed in abundance in sample A1 by $\gamma$-irradiation. The fact that both the two oxygen-deficiency-related PL bands (2.7 and 4.3 eV) are observed at a significant level in all the samples (except sample P) regardless of the sample category indicates that high total dose or high-dose rate $\gamma$-irradiation has a chance to break apparently normal silicon–oxygen bonds and to displace oxygen out of its normal position, i.e., high-dose (rate) irradiation can cause radiolysis ($Si-O-Si \rightarrow Si-Si + O$ (interstitial) and $Si-O-Si \rightarrow Si-O^+ + Si$). Under high-dose irradiation, bond breaking and the associated oxygen diffusion occurs at silicon–oxygen bonds other than point-defect sites (precursor sites).
Finally, in our previous work, we reported ten PL bands at 1.45, 1.8, 1.9, 2.15, 2.25 (two types, FWHM: $\sim 0.4$ eV, $\tau$: $\sim 25$ ns and FWHM: $\sim 0.2$ eV, $\tau$: $\sim 300$ ns), 2.7, 3.08, 3.15, and 4.3 eV in various as-grown and $\gamma$-irradiated samples, including measurements of PL excitation spectrum, PL decay lifetime, and temperature dependence. From the optical characteristics of the PL band, we were able to discover a trend, i.e., some kind of oxygen-deficient or oxygen surplus-associated defect centers are associated with the formation of PL bands. Based on these results, we suggest an origin structure model of the PL band [14–20,32–34]. Generally, the 2.7 eV and 4.3 eV PL intensities are strong in the oxygen-deficiency-type sample, and they are observed together. Therefore, it is our conclusion the origin of the two PL bands is identical, i.e., the two PL bands are transitions from the excited state to the ground state of the oxygen vacancy. However, in the after the heat treatment sample, we did not observe the 4.3 eV PL band, though we did observe the 2.7 eV PL band. From these results, we suggest that there is no common origin of these two PL bands, i.e., the oxygen vacancy is proposed as the origin of the 2.7 eV PL band, while it is not viewed as the origin of the 4.3 eV PL band [22]. This is important to understanding the emission mechanism of these two PL bands.

As described above, it is clear that the various defects and PL bands are formed in silica glass by $\gamma$-irradiation (especially in the oxygen-deficiency-type samples). However, the origin of these PL bands is not clear, including 3.9 eV PL band. Despite much effort, we were unable to reach an unambiguous conclusion and thus our ideas concerning these origins are still only a hypothesis. Although a further investigation is necessary to clarify the oxygen-deficit structures induced by the high-dose $\gamma$-irradiation, it is clear that high-dose $\gamma$-irradiation can be a useful technique to induce structural modification in a-SiO$_2$.

There is the E$^\prime$ center (the 5.8 eV absorption band) as a point-defect which has not been examined as a possible PL emission origin in silica glass. Therefore, it is necessary to examine the relation between the 3.9 eV PL band and the E$^\prime$ center. The E$^\prime$ center is one of the oxygen deficient-type defects, and there is a high probability of this defect forming with the oxygen vacancy. Therefore, it is important to make a sample with only the E$^\prime$ center. The results of our work increase the need to clarify whether the E$^\prime$ center is connected with the origin of the generation of the 3.9 eV PL band. In order to realize it, it is necessary to make a sample with special processing [35]. In order to understand the characteristics of the oxygen-deficiency-type defect, it is necessary to examine the electronic state of various oxygen-deficient-type defects. Of course, it is also necessary to examine the oxygen-associated defect centers (NBOHC, peroxy radical, small peroxy radical, and peroxy linkage). This is a problem for further study.

6. Conclusion

In this paper, we have demonstrated how to generate the PL band induced by $\gamma$-irradiation in high-purity various type silica glass. We observed a new PL band at approximately 3.9 eV only in high-dose $\gamma$-irradiated oxygen-deficient-type silica glass with the highest oxygen-deficient-associated defect centers [oxygen vacancy, E$^\prime$ center and E$^\prime\beta$ center]. The origin of the 3.9 eV PL band is not clear from the results of this experiment, but at least we can say that some kind of oxygen-deficient-associated defect centers are associated with the formation of this PL band. This study should be useful in clarifying the relation of the PL band to oxygen-deficient-associated defect centers, and in understanding the structural defects in silica glass.

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