

OH-content dependence of fractoluminescence spectra in silica glass

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The effect of OH content on fractoluminescence spectra in silica glasses was investigated. The spectra consisted of the 1.9- and 2.7-eV bands. The intensity of the 2.7-eV band was larger in lower OH samples. This is because the oxygen-deficient center (ODC) can be more easily created on the fracture surface of silica glasses with lower OH content. Moreover, silica glasses containing little OH have preexisting ODC's, and they are excited by fracture to emit the 2.7-eV photons. The origin of the preexisting ODC's and the ODC formation mechanism at fracture of silica glasses are discussed. [S0163-1829(96)03937-9]

I. INTRODUCTION

Synthetic silica glass has an excellent optical transparency, and is used as a material for optical fibers in telecommunication, and optical components for excimer laser in ultra large scale integration (ULSI) processes. However, various defect centers are induced by the irradiation of UV laser,¹⁻⁸ x ray,⁸⁻¹⁰ and γ ray.^{3,4,11-14} These defects degrade the optical transparency of the silica glass, and many works have been done to clarify the defect formation processes and to reduce the number of the induced defects.

Mechanical stimulus also creates defects in silica glass.¹⁵⁻¹⁹ Hibino and Hanafusa^{17,18} reported the defect formation in silica glasses by fiber drawing. On the dynamical processes of mechanical interaction, emission of electrons, ions, neutral particles, and photons is caused, and such a phenomenon is called fractoemission.²⁰⁻²⁶ Fractoemission is closely related with the dynamical processes on the fracture surface or the damaged surface of silica glass. We have studied photon emission at fracture of silica glass, and named the emission as fractoluminescence.²⁵

In a previous paper,²⁵ we reported time-resolved fractoluminescence spectra in silica glass. Two emission bands were observed in the spectra: the 1.9- and 2.7-eV bands. The energy position and the time response of the two bands were similar to those of photoluminescence in silica glass.²⁷⁻²⁹ On the photoluminescence spectra in silica glass, the 1.9-eV band is assigned to be related to the relaxation of some oxygen excess center, and one of the reliable candidates is the nonbridging oxygen hole center (NBOHC),^{4,28-30} while the 2.7-eV band is assigned to the relaxation luminescence of the oxygen deficient center (ODC).^{4,6,31,32} NBOHC can be created by the scission of the Si-O-Si bond. On the other hand, ODC can be created by the surface rearrangement of the neighboring two E' centers created by the breaking of the Si-O bonds, or by the direct ejection of the oxygen atom. Thus we assigned the 1.9- and 2.7-eV bands of fractoluminescence in silica glass to be due to the relaxation of NBOHC and ODC created and excited on the fracture surface.

It is well known that the contents of preexisting defect centers are strongly affected by the production conditions, and the preexistence of the ODC depends on the OH content in silica glasses.⁴ Moreover, the OH content is one of the

dominant factors to determine the physical properties, especially the mechanical flexibility, of silica glasses. Kobayashi *et al.*³³ reported that Young's modulus was smaller in higher OH silica glasses, that is, the network of the Si-O-Si bonds was more flexible in higher OH silicas. Kuzuu⁷ studied the OH-content dependence of the excimer-laser-induced absorption in type-III fused silicas. He reported that the laser-induced 5.8-eV absorption band was larger in lower OH silica glasses, and explained the result with the mechanical flexibility of the Si-O network.

In this paper, we investigate fractoluminescence spectra in silica glasses with different OH contents, and discuss the formation and excitation process of the ODC. Especially, the effect of the hydroxyl groups on the cleavage of the Si-O-Si bonds is explained.

II. EXPERIMENTAL PROCEDURE

Experiments were carried out on three kinds of commercially available silica glasses, ES, ED-A, and ED-B, trademarks of Nippon Silica Glass Co. Ltd. Samples ES were synthesized directly by flame hydrolysis of SiCl_4 . Samples ED-A and ED-B were manufactured by the vapor-phase axial deposition (VAD) method.³⁴ According to the manufacturer's analysis using infrared (IR) spectra, ED-B contained almost no hydroxyl groups, i.e., ≤ 1 ppm which was the detecting limit, while ED-A and ES contained about 70 000 ppm. The properties of ES are almost the same as those of Spectrosil, trademark of Thermal Syndicate Ltd., which were used in a previous paper.²⁵ Optical absorption spectra of the samples were measured using a Hitachi U-3000 spectrophotometer. Photoluminescence spectra were measured with the irradiation of the KrF line of an excimer laser (a MPB Technology PSX-100).

The experimental apparatus was the same as that in a previous paper.²⁵ Samples of $2 \times 10 \times 25$ mm³ were fractured by the three-point-bending method in a vacuum chamber at 1.3×10^{-5} Pa at room temperature. Fractoluminescence spectra were measured with an optical multichannel analyzer attached to a spectrometer. The spectra were not corrected for the spectral sensitivity of the detecting system.

Time response of the fractoluminescence intensity was measured using a photomultiplier and a photon counter, and the gate time was set to 10 μs . It is expected that there are

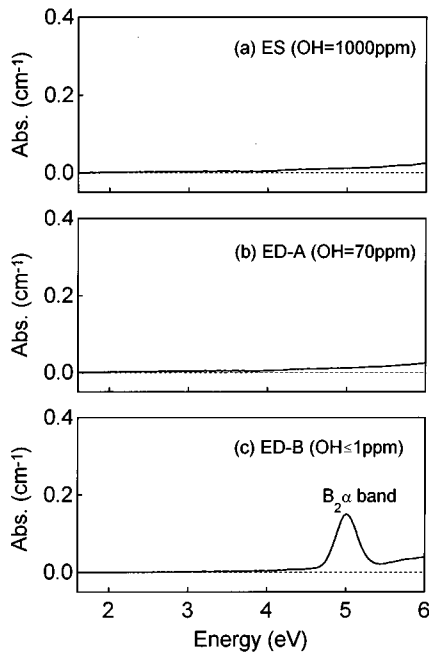


FIG. 1. Optical absorption spectra in silica glasses with different OH contents: (a) 1000 ppm, (b) 70 ppm, and (c) ≤ 1 ppm.

two emission bands in the fractoluminescence spectra: the 1.9- and 2.7-eV bands. To separate the energy range of the emitted photons in the time response measurement, an optical sharp-cut filter was inserted just in front of the photomultiplier; the first filter (Sigma Koki SCF-560) transmitted photons of $h\nu < 2.2$ eV, and the other one (Asahi Spectra TAX304A) transmitted photons in the energy range of 2.4–3.2 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows optical absorption spectra in silica glasses. ES and ED-A have no absorption peak in the region of 1.8–6.0 eV, while a large peak was observed at 5.0 eV in ED-B. Two kinds of 5.0-eV absorption bands are known in silica glasses: the $B_{2\alpha}$ and $B_{2\beta}$ bands.⁴ Tohmon *et al.*³¹ reported that the peak energy and full width at half maximum (FWHM) of the $B_{2\alpha}$ band were 5.02 and 0.35 eV, while those of the $B_{2\beta}$ band were 5.15 and 0.48 eV. In our result, the peak energy and the FWHM of the absorption band in ED-B were 5.01 and 0.31 eV. These values are in good agreement with those of the $B_{2\alpha}$ band. Moreover, by the irradiation of the 5.0 eV band in ED-B with the KrF line of the excimer laser, the 2.7- and 4.4-eV emission bands were observed which were related to the relaxation of the $B_{2\alpha}$ band. Thus we can say that the 5.0-eV absorption in ED-B is the $B_{2\alpha}$ band, and is assigned to be due to the ground-to-triplet excitation on ODC.³² That is, ED-B contains preexisting ODC's created in the manufacturing processes.

Figure 2 shows fractoluminescence spectra in silica glasses with different OH contents. All samples exhibit two emission bands around 2.7 and 1.9 eV, the same as in the previous paper.²⁵

To observe the time response of each emission band, total emission was separated with an optical sharp-cut filter as described in the previous section. The result in ED-A is

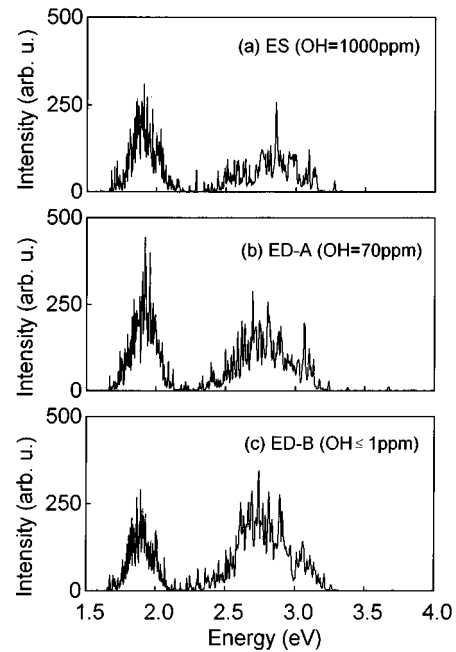


FIG. 2. Fractoluminescence spectra in silica glasses with different OH contents: (a) 1000 ppm, (b) 70 ppm, and (c) ≤ 1 ppm.

shown in Fig. 3. The solid line is a result of curve fitting with an exponential function. A slow component was mixed in the tail of the exponential decaying component in the 1.9-eV band, and a fast decaying component was observed before the slow exponential decay in the 2.7-eV band. These should be a contribution of the stray light from the other emission band and they are too weak for detailed analysis. Thus we focus on the main exponential decaying component in each decay curve. The decay time of the main exponential decaying component was about 35 ± 5 μs for the 1.9-eV band, and

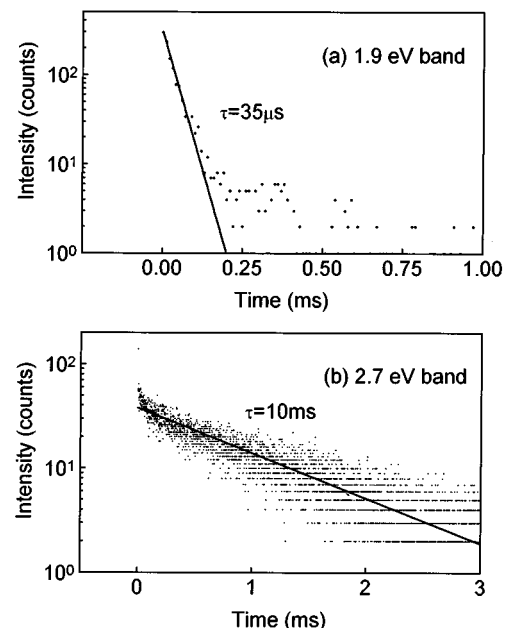


FIG. 3. Time response of the fractoluminescence in ED-A: (a) 1.9-eV band and (b) 2.7-eV band.

about 10 ± 1 ms for the 2.7-eV band. The values of decay times were the same in ED-B and ES within the experimental error.

In case of photoluminescence in silica glass, decay time of the 1.9-eV band is reported to be $14 \mu\text{s}$ by Nishikawa *et al.*²⁸ and $17 \mu\text{s}$ by Kawaguchi and Yamamoto.²⁶ Decay time of the 2.7-eV band is about 10 ms.²⁶⁻²⁸ For the 2.7-eV band, the decay time in fractoluminescence is in good agreement with that in photoluminescence, while the observed decay time of the 1.9-eV band in fractoluminescence is about twice of that in photoluminescence. In the above experiment, the gate time of the photon counter was set to $10 \mu\text{s}$ which was comparable to the observed decay time for the 1.9-eV band, $35 \mu\text{s}$. Thus the value of $35 \mu\text{s}$ should be affected by the artifact of the measuring system. With smaller gate time, scatter of the data became too large for data analysis. Moreover, it is expected that the process of fracture in silica glasses will take time of the order of microseconds to tens of microseconds, and this time interval will make the observed decay time longer. Considering these situations, we can say that the decay time of the 1.9-eV band in fractoluminescence corresponds to that in photoluminescence, too. Thus it is confirmed that the two emission bands in fractoluminescence spectra in ES, ED-A, and ED-B are also due to the relaxation of NBOHC and ODC, as is the case in Spectrosil.²⁵

Next, we compare the intensities of the two bands in three kinds of samples shown in Fig. 2. Bearing in mind the scatter in the data, the intensity of the 1.9-eV band was almost the same amongst samples containing different amounts of hydroxyl groups. The intensity of the 2.7-eV band, on the other hand, was larger in lower OH samples.

Reproducibility of the absolute intensity in each emission band was not so good, because the fracture event on the macroscopic scale was difficult to control. On the other hand, the intensity ratio between the two bands is thought to be less affected by the fluctuation in each fracture event, because the change of the absolute intensity will be canceled. To make the OH-content dependence of the 2.7-eV band more clearly, we normalized the integrated intensities of the 2.7-eV band with those of the 1.9-eV band, and plotted the intensity ratios in three kinds of silica glasses. The result is shown in Fig. 4. The value of $I_{2.7 \text{ eV}}/I_{1.9 \text{ eV}}$ was larger in samples with lower OH contents, and this tendency was prominent in ED-B which contained few hydroxyl groups.

We can explain the above result as follows. A unit structure of a silica glass is SiO_4 ; four oxygen atoms compose a tetrahedron with one silicon atom at the center. Because silica glass is an amorphous material, unit structures of tetrahedra connect in a disordered way and construct a network of Si-O-Si bonds. Due to the randomness of the network, some of the Si-O-Si bonds should be in the nonideal state. That is, the bond angle of Si-O-Si is far from the equilibrium value, 144° .

ES contains a lot of hydroxyl groups, i.e., 1000 ppm, resulting from the manufacturing process, and some of the Si-O-Si bonds are broken and terminated in the form of Si-OH. Thus the number of the unstable Si-O-Si bonds is reduced, the stress accumulated in the glass network is relaxed, and the flexibility of the glass must increase. In ED-A with the OH content of about 70 ppm, the number of strained Si-O-Si bonds will be reduced in the same manner.

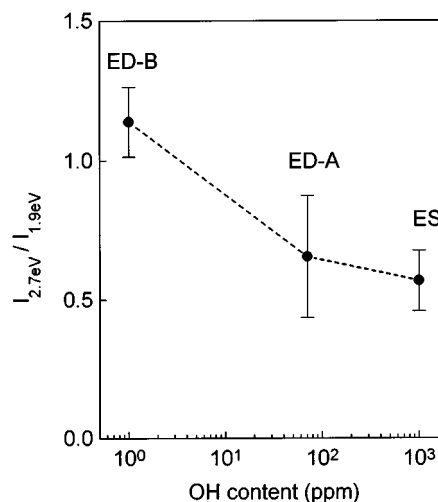


FIG. 4. OH content dependence of the intensity ratio between the 2.7- and 1.9-eV band.

On the other hand, ED-B contains little hydroxyl groups and impurities. There is no candidate to modify the network structure and relax the strained Si-O-Si bonds. Thus many Si-O-Si bonds remain strained. Moreover, during the manufacturing process, some of the strained Si-O-Si bonds are unable to support the stress and are broken to create defect centers. Defect centers with lonepair electrons, for example E' center and NBOHC, will react to form a more stable structure in the manufacturing process. Some oxygen atoms are dissolved from the Si-O-Si bonds in the dehydration process, resulting in the creation of the $\text{Si} \cdot \cdot \cdot \text{Si}$ structure, i.e., ODC. Because ODC is electrically neutral, ODC's are more stable than the defect centers with lonepair electrons, and many ODC's remain. This is the reason the $B_2\alpha$ band was observed in photoabsorption spectra in ED-B.

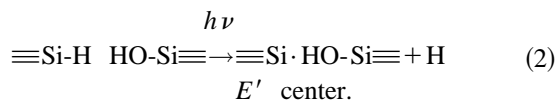
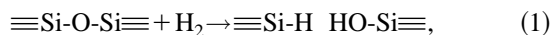
Gibbs *et al.*³⁵ investigated the molecular orbital calculation in silica polymorphs, and reported that the energy per Si-O bond varies only within 0.1 eV by the change of the bond angle distribution $120^\circ \leq \text{Si-O-Si} \leq 180^\circ$. However, the stability of the total glass network cannot be considered only with the change of the single bond energy. A strain of one bond will influence the structural stability of the glass network in a certain area. The resulting increase of the free energy of the glass network in the area can be much larger than the change of the single bond energy. Thus it should be that the energy to be accumulated at the instant of bond cleavage is large enough to accelerate the drastic bond breaking and defect formation.

Devine and Arndt^{3,11} investigated γ -ray- and excimer-laser-induced defect formation in densified silica glasses. They reported that the number of induced defects is much larger in densified silicas than that in undensified ones, showing that the strained Si-O-Si bonds are more easily broken by irradiation.

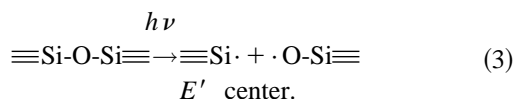
Kuzuu⁷ reported the example of the result showing the relationship between the OH content of the silicas and the resistivity against irradiation. He investigated excimer-laser-induced absorption spectra in type-III fused silicas with different OH contents. He reported that the induced 5.8-eV absorption band was smaller in samples with larger OH

contents, and was below the detection limit in samples with 1160 ppm of hydroxyl groups. The 5.8-eV band is assigned to be due to the E' center.⁴ He modeled two processes for the creation of the E' center.

(i) Creation of the Si-H HO-Si structure, a precursor of the E' center,⁵ by the reaction of the unstable Si-O-Si bonds with the hydrogen molecules in the manufacturing process, followed by the breaking of the Si-H HO-Si structure:

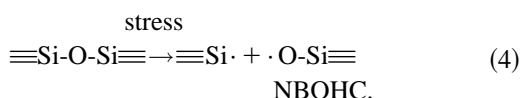


(ii) Breaking of the Si-O-Si bonds directly:



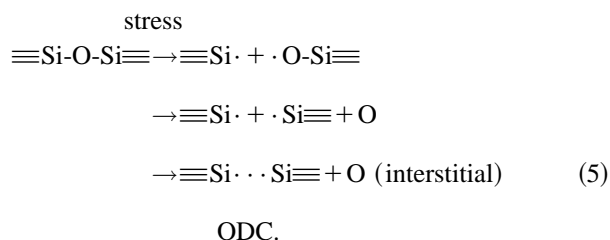
Kuzuu explained the result of the laser-induced 5.8-eV absorption band in relation to the flexibility of the Si-O-Si bonding network. Because the network of the Si-O-Si bonds is more flexible and stable in higher OH samples, the formation of the precursor by the process (1) will be suppressed, and the E' center formation will also be reduced. Moreover, the direct bond breaking by the process (3) will be also suppressed in higher OH samples.

In our assignment on the fractoluminescence spectra in silica glass, the 1.9- and 2.7-eV bands are due to relaxation of NBOHC and ODC created and excited on the fracture surface. NBOHC will be created by breaking one of the Si-O-Si bonds as follows:

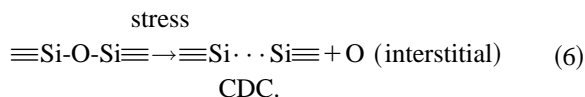


In the creation of ODC, both of the Si-O-Si bonds on the oxygen atom must be broken in the following ways.

(i) Successive breaking of Si-O bonds and surface reconstruction of the neighboring two E' centers:



(ii) Direct ejection of the oxygen atom:



As for the 1.9-eV emission band related to the NBOHC's, the intensity is almost the same in all types of silicas. This result is not so surprising, since the number of bond breaking process (4) at the fracture surface is, to first order, the same in all types of silicas.

On the other hand, more drastic bond breaking is necessary to break both the Si-O-Si bonds and create ODC by the processes (5) and (6). In samples with lower OH content, many Si-O-Si bonds are strained and rigid, and both of the Si-O-Si bonds will be broken more easily by applying the stress. Therefore, more ODC's will be created and excited in the fracture process and the intensity of the 2.7-eV emission band will become larger in lower OH silica glasses.

Moreover, ED-B contains preexisting ODC's created in the manufacturing process while ED-A and ES do not, as described above. The preexisting ODC's in ED-B will be also excited during fracture, and emit photons of 2.7 eV. This emission should work to enhance the 2.7-eV band in fractoluminescence spectra.

IV. CONCLUSION

We have investigated fractoluminescence spectra in silica glasses with different OH contents. All samples had two emission bands at 1.9 and 2.7 eV in the spectra. The intensity of the 2.7-eV band was larger in lower OH silicas, while that of the 1.9-eV band was almost the same in all types of silicas. The difference of the intensity of the 2.7-eV band comes from the different number of ODC's, partly due to the pre-existing ones, and partly due to what are created at fracture. That is, silica glasses with little OH contain preexisting ODC's created in the manufacturing processes. Moreover, in lower OH silicas, due to the lack of the hydroxyl groups, many Si-O-Si bonds in the glass network are strained, and drastic bond breaking occurs more easily and creates ODC's.

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