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Time-resolved fractoluminescence spectra of silica glass in a vacuum and nitrogen atmosphere

Y. Kawaguchi
Chugoku National Industrial Research Institute, 2-2-2, Hiro-Suehiro, Kure, Hiroshima 737-01, Japan

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Time-resolved fractoluminescence spectra of silica glass are investigated at room temperature in a vacuum and nitrogen atmosphere. Two emission bands are seen in the spectra: the 1.9- and 2.7-eV bands. The 1.9-eV band peaks around 5 μs, and decays around 100 μs after the instant of fracture. The 2.7-eV band rises in about 50 μs, peaks around 500 μs, and decays in several tens of milliseconds after fracture. The energy position and the time response of the two bands are similar to those in the photoluminescence of silica glass. The role of the surface defect centers to the fractoluminescence of silica glass is discussed.

I. INTRODUCTION

Silica glass is a widely used material for optical components, due to its excellent optical transparency. Recently, the needs of silica glass with high quality have become large for a material of optical fiber which plays a key part in optical telecommunication.

In order to answer these demands, many works have been carried out to clarify the fundamental properties of silica glass by many experimental techniques, especially on the properties of defect centers: mechanical strength experiments,[1–4] ESR,[5–9] NMR,[10–12] optical absorption,[6,8,13–19] photoluminescence,[8,13,14,16,19–24] cathodeluminescence,[25–28] fractoemission,[29–35] and so on.

Stathis and Kastner[21] reported time-resolved luminescence spectra of silica glass under 7.9 eV photoexcitation, and showed emission bands at 1.9, 2.2, 2.7, and 4.3 eV. The 1.9-eV band decays with a time constant of about 10 μs while the 2.7-eV band rises in about 50 μs and decays with $\tau_d = 10$ ms. By ESR measurements and molecular-orbital calculation, Tohmon and his co-workers[15,16] assigned the 2.7-eV band to the luminescence by triplet-to-ground state relaxation on single oxygen vacancy. On the other hand, the 1.9-eV band is related to the relaxation of the nonbridging oxygen hole center (NBOHC), though many models are submitted and detailed processes are still in discussion.[8,14,18,19,23] Nishikawa and his co-workers[23] reported 1.9-, 2.7-, and 4.3-eV bands of photoluminescence spectra at room temperature, discussed the influence of the oxygen stoichiometry and OH concentrations, and concluded with similar assignment of the spectra as those by Tohmon *et al.*[15,16]

On the other hand, many experimental works have been reported on the role of mechanical stimulus. Hibino and his co-workers[6,13,22] reported that many kinds of defect centers are created due to mechanical stress during fiber drawing, and the centers degrade the optical transparency of the fiber. Ohki and his co-workers[9] reported by ESR measurement that Si—O—Si strained bonds are created under mechanical stress, and that the strained bonds work as the precursors of the E' center ($\equiv$Si$\cdot$) and NBOHC ($\equiv$Si—O$\cdot$) at fracture of silica glass, where "$\equiv$" denotes the three back bonds to oxygens and "$\cdot$" signifies an unpaired electron.

Moreover, electrons, ions, neutral particles, and photons are emitted at fracture of silica glass, and they are all known as fractoemission.[29–35] Dickinson and his co-workers[30] reported the time response of electron emission, ion emission, and photon emission at fracture of silica glass. They also measured mass analysis of positive ion emission with a time-of-flight mass spectrometer,[31] and reported the masses of 16, 28, 44, and 72, which they assigned to O^+, Si^+, SiO^+, and Si_2O^+. But many things are still unknown on the mechanism of fractoemission.

To clarify the role of defect formation and relaxation processes on the fracture surface of silica glass, we focus our interest on the photon emission at fracture of silica glass, and we define the emission as fractoluminescence, in a narrow meaning in comparison to the term fractoemission which includes emission of all kinds of particles and photons. This paper reports the time-resolved fractoluminescence spectra of silica glass, and compares the spectra with those of photoluminescence. Time correlation of fractoluminescence with charged particle emission is examined, the influence of nitrogen gas atmosphere to the luminescence is investigated, and the role of the defect centers on the fracture surface to fractoluminescence is discussed.

II. EXPERIMENT

We discuss here the experimental apparatus for measuring photon emission spectra at fracture of silica glass. Because fractoemission is much influenced by the surrounding gas conditions, we executed the fracture experiment in a vacuum chamber, and gas pressure was controlled by pumping the chamber with a turbomolecular pump and flowing a pure gas at a constant rate with a variable leak valve. Oxygen and water molecules can strongly modify the active fracture surface of silica glass by chemical reaction with the dangling bonds and can complicate the experimental results, so that we used nitrogen gas with a purity of 99.999% as an atmosphere. All the experiments were executed at room temperature.

A silica glass specimen of Spectrosil with a dimension of $10 \times 25 \times 2$ mm^3 was set to the three-point bending ap-

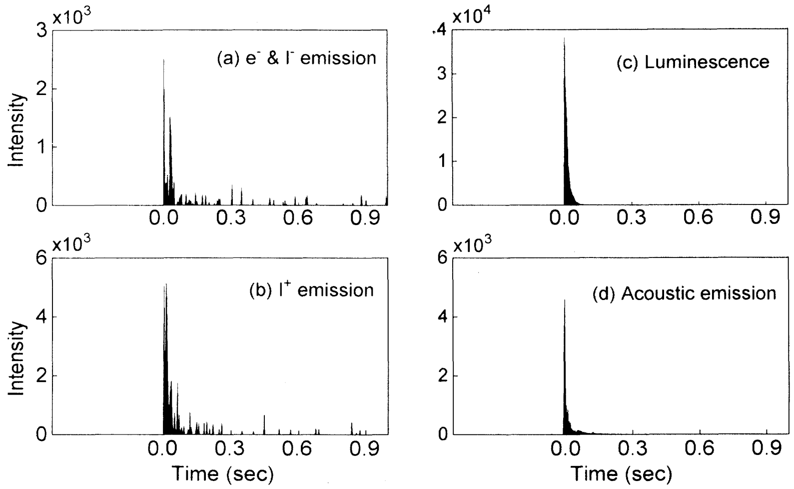

FIG. 1. Time response of fractoemission from silica glass at 6.7×10^{-6} Pa: (a) negative charge emission, (b) positive charge emission, (c) luminescence, and (d) acoustic emission.

paratus, and it was fractured at the center of the chamber. A compact acoustic emission (AE) sensor was mounted on the load applicator, and the AE signal at fracture of silica glass was also monitored.

For measuring the fractoluminescence spectra, the optical multichannel analyzer (Hamamatsu Photonics C4653-011G) attached to the spectrometer (JASCO CT-25C) was set at the back of the quartz lens and the sapphire viewport. The focal length of the spectrometer is 25 cm. The optical multichannel analyzer has an image intensifier with the two microchannel plates which intensifies the incident photon signal by 10^6. The first rise-up signal of AE at the instant of the fracture was used for triggering the optical multichannel analyzer, and the time resolution was about 500 ns in time-resolved spectra measurement.

Because fractoluminescence is a one shot event and the intensity is very small, much care was taken to achieve a one shot measurement with high efficiency. First, the grating of the spectrometer was changed to a very coarse one, 150 lines/mm, so that the luminescence with a large spectral range could be measured at one time. Next, the slit width was set to 2 mm in order to get the incident photon signal with high efficiency at the sacrifice of the bandwidth to about 20 nm, 0.10 eV at 2.5 eV. Last, the linear image sensor and the photocathode of the image intensifier were cooled to $-15\,°\mathrm{C}$ and $-25\,°\mathrm{C}$, preventing the influence of thermal noise. In this way, we could achieve the sensitivity of the optical multichannel analyzer almost similar to that in the photon-counting method.

In the case of measuring time response of the total luminescence intensity, a photomultiplier (Hamamatsu Photonics R2801) was attached just behind the viewport of the vacuum chamber. The emitted photon was detected with the photomultiplier, and measured with a photon counter (Hamamatsu Photonics C2550). The gate time of the photon counter was set to 10 μs. Positive and negative charges were detected with two channeltron detectors (Murata EMW-6081B), measured with a charge sensitive amplifier, and compared with the fractoluminescence.

III. RESULTS

Figure 1 shows an example of the time response of the fractoemission from silica glass at 6.7×10^{-6} Pa. Negative charge emission, positive charge emission, luminescence, and acoustic emission are measured at one time. No signal is detected during plastic deformation of the specimen, and the signals rise at the very instant of the fracture. Charged particles are emitted randomly and intermittently, and continue for hundreds of milliseconds after the end of the fracture. On the other hand, the luminescence and acoustic emission decay instantaneously after the fracture. This result means that fractoluminescence does not originate from the ions emitted from the fracture surface with a delay of several hundreds of milliseconds after fracture.

Figure 2 shows a typical example of the time integrated fractoluminescence spectrum measured at 1.3×10^{-5} Pa. The spectrum has not been corrected for the spectral sensitivity of the detecting system. Both small intensity of the emitted photon and large gain of the detector result in the scattering of the data, so that discussion on the fine structure of the spectrum is not made here. There exist two emission bands in the spectrum. The first band is situated around 1.9 eV, and the second one is around 2.7 eV.

Figure 3 shows the time-resolved spectra of photon emission from silica glass. In this experiment, the spectra

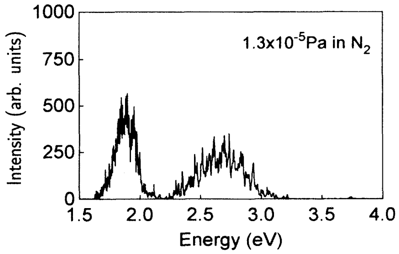

FIG. 2. Time integrated fractoluminescence spectrum of silica glass at 1.3×10^{-5} Pa.

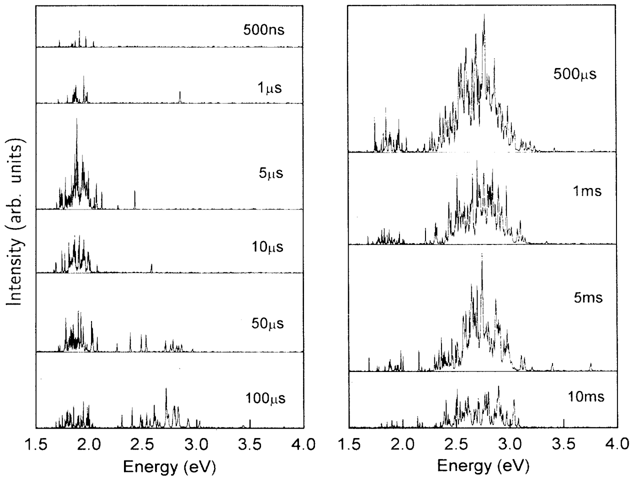

FIG. 3. Time-resolved fractoluminescence spectra of silica glass at 1.3×10^{-5} Pa.

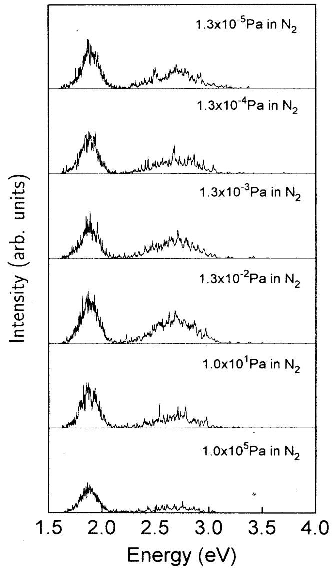

FIG. 5. Pressure dependence of time integrated fractoluminescence spectra of silica glass in N_2.

were measured at 1.3×10^{-5} Pa, and the ratio of the gate time to the delay time was fixed to 0.2. The 1.9-eV band rises within 500 ns after fracture, peaks around 5 μs, and decays around 100 μs. On the other hand, the 2.7-eV band begins to grow at about 50 μs after fracture, peaks around 500 μs, and decays in the order of tens of milliseconds.

To investigate the influence of the surrounding gas to the fractoluminescence, the time response of total luminescence intensity is measured at various pressures in N_2, and the results are shown in Fig. 4. Because the signal is a mixture of the 1.9- and 2.7-eV bands, it shows a sum of two decay components. The fast component decays with a time constant comparable to the gate time of 10 μs in photon-counting measurements. On the other hand, the slow component rises as shown with a small bump, and decays with a time constant of about 10 ms. The time constants of both components are almost independent of the pressure. The intensities of both components become weaker with increasing pressure, and the slow component almost vanishes at atmospheric pressure, namely, 1.0×10^{5} Pa.

Figure 5 shows time integrated fractoluminescence spectra at various pressures in N_2. The energy positions of the two bands do not change with pressure, and the intensities become weaker with increasing pressure, especially in the case of the 2.7-eV band above 1.3×10^{3} Pa. The pressure dependence of the luminescence intensity for each band is calculated from Fig. 5, and the results are shown in Fig. 6. The dotted lines are guides to the eye. In spite of the large scattering of the data, it can be

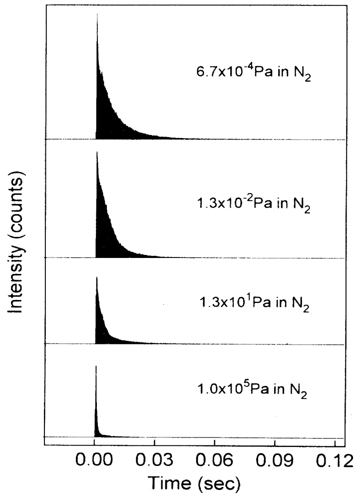

FIG. 4. Pressure dependence of fractoluminescence of silica glass in N_2.

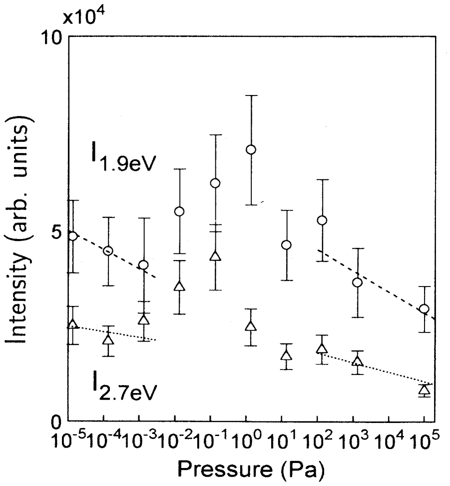

FIG. 6. Pressure dependence of the luminescence intensities of the 1.9- and 2.7-eV bands in N_2.

seen that the intensities of both bands decrease with increasing pressure in the pressure range below 10^{-3} Pa and above 10^3 Pa. Especially, the rapid decrease of the 2.7-eV band at 1.0×10^5 Pa corresponds to the vanishing of the slow component in Fig. 4. On the other hand, there is a small peak in each band whose height is comparable to the error bars at $10^{-1}-10^{0}$ Pa.

IV. DISCUSSION

We have successfully measured the time-resolved fractoluminescence spectra of silica glass. Now we discuss the mechanism of the fractoluminescence.

Besides luminescence, electrons and ions are emitted at fracture of silica glass. The first candidate for the fractoluminescence is the relaxation luminescence of the ions emitted from the fracture surface. As shown in Fig. 1, the ion emission lasts several hundreds of milliseconds after the end of the fracture. Dickinson and his co-workers[30–32] proposed a model that the local charge distribution caused by the bond scission creates a strong local electric field, and that the electric field accelerates and emits charged fragments of the Si—O chains from the fracture surface. Due to the small mobility of electrons and ions in the glass, the local charge distribution does not neutralize soon, so that the ion emission lasts for a long time after fracture. On the other hand, fractoluminescence decays within 100 ms. The difference of the time response between the ion emission and the fractoluminescence rejects the first candidate.

The second candidate is the blackbody radiation[29] by local heating on the fracture surface. Because the fractoluminescence spectra do not obey the Planck's formula and have a structure of two bands, this possibility is rejected.

The third candidate is the relaxation luminescence of the surface defect centers. As shown in Figs. 2 and 3, the fractoluminescence consists of the 1.9- and 2.7-eV bands. The 1.9-eV band rises within 500 ns, peaks around 5 μs, and decays around 100 μs. The 2.7-eV band rises in about 50 μs, peaks around 500 μs, and decays in the order of 10 ms. The energy position and the time response of the two bands in the fractoluminescence show good agreement with those of the photoluminescence.

In the photoluminescence spectra, the 1.9-eV band is considered to be associated with the relaxation of NBOHC, but the details are still in discussion.[8,14,18,19,23,24] The scission of the Si—O bonding causes dangling bonds of Si and O, namely the E' center and NBOHC, with high density on the fracture surface of silica glass as

$$\equiv\mathrm{Si{-}O{-}Si}\equiv\;\rightarrow\;\equiv\mathrm{Si}\cdot+\cdot\mathrm{O{-}Si}\equiv\;.$$

Thus we assign the 1.9-eV band in the fractoluminescence as being related to the relaxation of NBOHC.

On the other hand, the 2.7-eV band in the photoluminescence is assigned to triplet-to-ground state relaxation on the single oxygen vacancy.[15,16] There are two possible ways to create the oxygen vacancy on the fracture surface under mechanical stress as follows.

(i) Successive breaking of Si—O bonds and surface reconstruction of the two neighboring E' centers, resulting in the creation of the oxygen vacancy and interstitial oxygen atom:

$$\begin{aligned}\equiv\mathrm{Si{-}O{-}Si}\equiv\;&\rightarrow\;\equiv\mathrm{Si}\cdot+\cdot\mathrm{O{-}Si}\equiv\\&\rightarrow\;\equiv\mathrm{Si}\cdot+\cdot\mathrm{Si}\equiv+\mathrm{O}\\&\rightarrow\;\equiv\mathrm{Si{-}Si}\equiv+\mathrm{O(interstitial)}\;.\end{aligned}$$

(ii) Direct knock-on of the oxygen atom:

$$\equiv\mathrm{Si{-}O{-}Si}\equiv\;\rightarrow\;\equiv\mathrm{Si{-}Si}\equiv+\mathrm{O(interstitial)}\;.$$

In either case, unstable oxygen atoms are created. Dickinson and his co-workers[30,31] reported O^+ emission which delays several tens of microseconds after fracture, which supports the existence of the unstable interstitial oxygen atom after fracture. The rise time of about 50 μs in the 2.7-eV band of fractoluminescence can be considered to the time of the population transfer between the singlet and triplet excited state by the intersystem crossing. Thus we make an assignment that the 2.7-eV band in the fractoluminescence is caused by the triplet-to-ground relaxation on the oxygen vacancy.

There is still another problem: how are the defect centers excited? We can point out two possibilities. One possibility is that the defect centers are excited directly during defect formation by the supplied mechanical energy. The other is that the defect centers created at fracture are excited by the collision of the emitted electrons and ions. In order to decide which process is dominant, we need to get detailed information on the rise-up process of the luminescence in the initial stage. In the measurement of the time-resolved spectra, the time resolution is about 500 ns, not short enough, so that we cannot determine the excitation process of the defect centers at this moment.

Moreover, we consider the contribution of the discharge of the surrounding nitrogen molecules[36] to the fractoluminescence. The luminescence by the discharge of gas molecules is known to have a large maximum at low vacuum, and decrease rapidly at high vacuum and near atmospheric pressure, according to Paschen's law.[37,38] Figure 6 shows that the luminescence decreases in the pressure range below 10^{-3} Pa, and the contribution of gas molecules to the fractoluminescence can be neglected in this high vacuum region. On the other hand, there is a small peak for each band at $10^{-1}-10^{0}$ Pa. This peak might be a contribution of the relaxation luminescence from the surrounding nitrogen molecules overlapped on the luminescence of defect centers, though the peak height is small and comparable to the error bar.

Except for the pressure range of $10^{-2}-10^{2}$ Pa, the fractoluminescence decreases with increasing pressure, so that we assume that the surface defect centers are relaxed nonradiatively by collision and adsorption of the nitrogen molecules. Sasaki[39] reported that the Ni film is coated on Si_3N_4 by scribing Si_3N_4 with a Cu stylus in the solution for Ni electrolytic plating under tribological stimulus, which he explained by mechanochemical reaction with the help of the surface charge. Similarly, it is expected that local charge distribution is created on the fracture surface of silica glass, and that it enhances the chemical reaction between the dangling bond and nitrogen molecules. Thus there might be a possibility that the nitrogen gas reacts chemically with the defect centers to create Si_xN_y and NO_x on the fracture surface of silica glass, and hinders the luminescence.

Lastly, the 4.3-eV band is well known in the photoluminescence spectra of silica glass, and it is thought to be related to the oxygen vacancy also.[23] We tried to observe the 4.3-eV band in the fractoluminescence measurement, but detected no signals. This might be due to the shortage of the time resolution in the operation of the optical multichannel analyzer, because the decay of the 4.3-eV band is very fast, less than 100 ns, in the photoluminescence. In order to check the existence of the 4.3-eV band exactly, we need to improve the trigger signal to a faster one, and it is a problem for the future.

V. SUMMARY

We have succeeded in measuring time-resolved fractoluminescence spectra of silica glass.

(i) Two bands are observed at 1.9 and 2.7 eV.

(ii) The energy position and time response of the two bands are similar to those in the photoluminescence of silica glass.

(iii) The 2.7-eV band is assigned to the relaxation luminescence of oxygen vacancy on the fracture surface of the silica glass, while the 1.9-eV band is to be related to the relaxation of NBOHC.

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