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Study of damage processes of silica by in situ hydrogen-ion-induced luminescence measurements

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Abstract

We have performed in situ measurements of luminescence from high and low OH silica glasses and a silica single crystal under H^+ irradiation. The luminescence spectra showed various emission bands assigned to intrinsic and irradiation-produced defects in silica. With increase of H^+ fluence, the intensity of the 2.7 eV band first increased and then gradually decreased, and which were respectively attributed to production of the $B_{2\alpha}$ oxygen deficient centers and their subsequent annihilation by defect clustering or Si precipitation. Such defect formation processes under H^+ irradiation were influenced by the amount of intrinsic OH in silica glass, i.e., irradiation-produced defects were more stable in the high-OH silica glass compared with the low-OH silica glass. The detailed analyses of the luminescence of silica single crystal indicated that the defect formation process after some amorphization of silica crystal is fundamentally the same as that in the low-OH silica glass.
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1. Introduction

Neutron or ion irradiation and radiation effects in silica glasses are one of the main concerns for their application as optical windows, insulators and optical fibers in fusion reactors as well as in fission reactors [1]. In order to investigate dynamic effects of in-reactor irradiation of silica, we have made in situ luminescence measurement of silica glasses induced by in-reactor irradiation. The in-reactor luminescence from silica was found to be a powerful technique to observe dynamic effects on the electrical property of silica, since the luminescence was directly associated with the electron excitation process under the irradiation. So far, we found that the luminescence mainly originates from the impurities such as defects in silica due to electron excitation during irradiation [2–4].

Under irradiation by high-energy ions, various types of defects such as B centers, E centers and non-bridging oxygen hole centers (NBOHC) are produced in silica not only by atomic displacement but also by electron excitation [5,6]. At the same time, the excited electrons are expected to induce luminescence related to the generated defects. Some authors have reported that the mechanism of defect creation under ion irradiation is influenced by the silica structure and content of OH impurity in silica [7,8]. Nevertheless, detailed effects of these factors on the damage process in silica are still open question. In the present study, we have carried out in situ measurements of luminescence from silica samples under the irradiation of hydrogen ions, to investigate the damage processes in silica single crystal and glasses with different OH contents.

2. Experimental

The samples used in this work were a low-OH fused silica glass (T-2030, OH content: 1 ppm) and a high-OH synthesized silica glass (T-4040, OH content: 800 ppm)

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of $10\times10\times0.1$ mm^3 produced by Toshiba Ceramics, Japan and a silica single crystal of $10\times10\times1$ mm^3 produced by Tateho Kagaku, Japan.

H^+ ions accelerated to 13 keV and mass analyzed were injected into the samples at room temperature through an aperture 8 mm in diameter with an incident angle of 90° to the sample surface. With the aid of differential pumping, the vacuum of the chamber during the irradiation was maintained below 1×10^{-5} Pa. The flux of incident H^+ ions monitored by a Faraday cup was 2.5×10^{13}/cm^2 s in the present irradiation experiment. The ion-induced luminescence was transmitted by optical fiber to a spectrometer (CP-200, JOBIN YVON) and a detector (OMA 1460, EG&G PRINCETON APPLIED RESEARCH).

3. Results

Fig. 1(a)–(c) respectively shows observed ion-induced luminescence spectra of the high-OH silica glass, the low-OH silica glass and the silica single crystal under irradiation by 13 keV H^+. Although the spectra are different among the samples and irradiation fluences, they consist of either/or all of four emission bands peaked at around 1.9, 2.2, 2.7 and 3.1 eV. Therefore each spectrum was decomposed into four Gaussian components as indicated in Fig. 1(d) and the intensity and FWHM of each component were plotted against H^+ fluence in Fig. 2. The 3.1 eV band was appreciable only in the low-OH silica glass but disappeared rapidly with increasing H^+ irradiation (Fig. 2(a)). The 1.9 eV band, the least intense, tended to decrease slightly and kept nearly constant for further H^+ irradiation for all samples. The 2.2 eV band dominated in the silica crystal at early stage of the irradiation, increased slightly, the gradually decreased with increasing irradiation fluence (Fig. 2(b)). On the other hand, the 2.2 eV band in the glasses was very weak with nearly constant intensity (not shown here). The 2.7 eV band, which was the most prominent ion-induced luminescence, rapidly increased, reaching a maximum. For high-OH silica, the peak appeared at a fluence around 2×10^{15} H^+/cm^2, and then gradually decreased with some indication of a second maximum at 1×10^{16} to a nearly saturated intensity above 1×10^{17} (Fig. 2(c-1)). In low-OH silica, the second maximum was observed very clearly (Fig. 2(c-2)). In the single crystal, a two peaked structure was also appreciable, but both peaked at much higher fluences than those for the glasses (Fig. 2(c-3)).

Fig. 2(d-1)–(d-3) shows the variation of full width at half maximums (FWHM) of the 2.7 eV band with H^+ fluence. One can note that FWHM shows two minimums at the same fluences for the intensity maximum. This suggests that there are two different characteristic bands peaked at 2.7 eV. Furthermore, the later appearing band in the high OH could be broken into more complex bands as seen in the increase of FWHM at higher fluences.

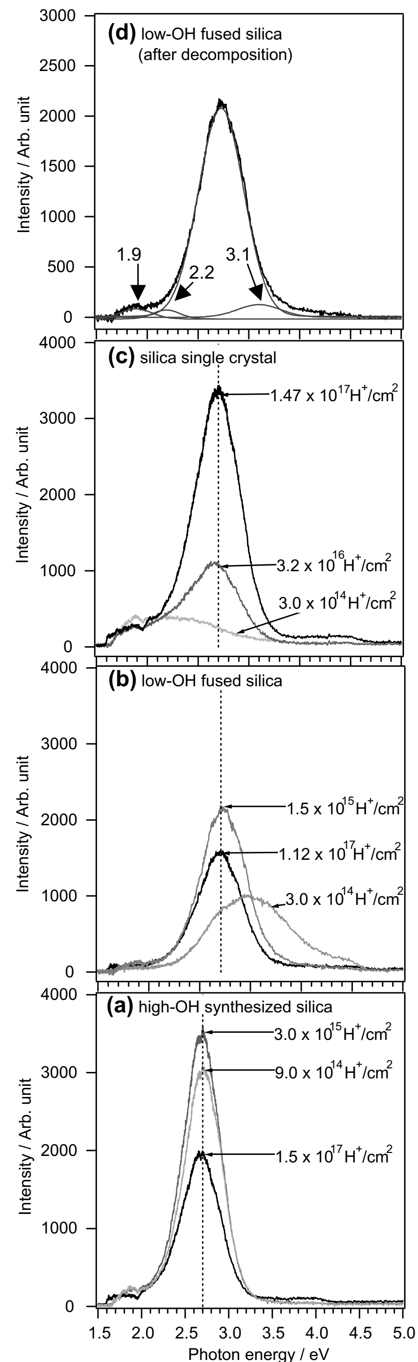

Fig. 1. Observed luminescence spectra of various types of silica samples at room temperature for three different fluences of 13 keV H^+ (a–c), and the decomposition of the luminescence spectrum into four Gaussians peaked at 1.9, 2.2 2.7 and 3.1 eV (d).

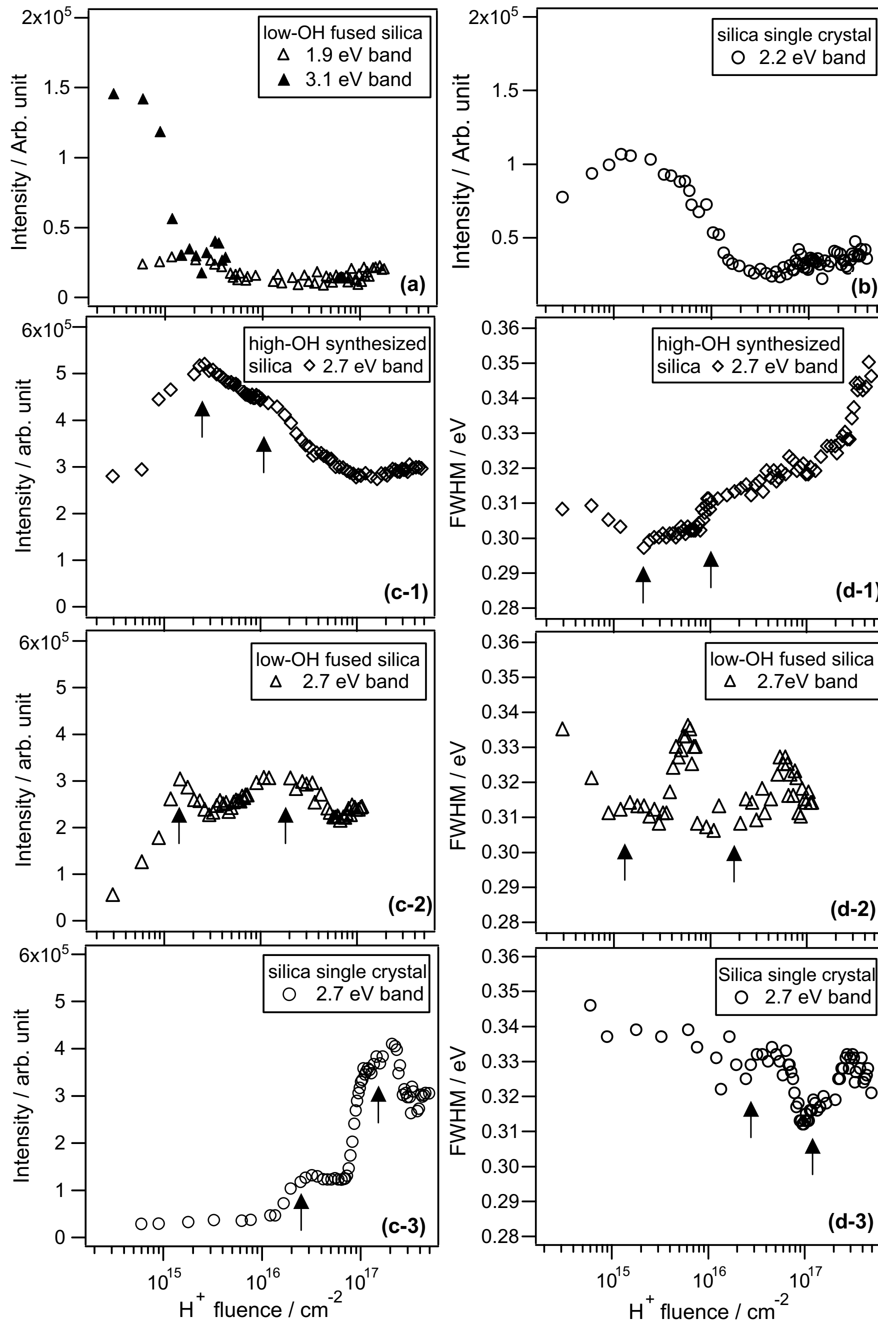

Fig. 2. Changes of the intensities of 3.1 and 1.9 eV emission bands (a), that of the 2.2 eV emission band (b) and changes of intensities and FWHMs of the 2.7 eV emission bands (c,d) with H^+ fluence.

4. Discussion

4.1. Origins of the emission bands

In the present H^+-induced luminescence spectra of silica glasses, we have observed emission bands centered at around 1.9, 2.2, 2.7 and 3.1 eV. At these energies, emission bands have already been observed in cathodo-, photo- and in-reactor luminescence spectra of silica glasses [2–4,9,10], and were attributed to the emissions of excitons and/or some point defects.

The NBOHC (non-bridging oxygen hole center) in silica glass is well known to give rise a characteristic PL peak at 1.9 eV [11,12], suggesting the present 1.9 eV emission band to be the NBOHC in silica.

The origin of the 2.2 eV band is not clear. But the peak is most likely due to F center in a silica crystal. This band was prominent only for the silica single crystal in the early stage of the irradiation and disappeared with increasing fluence, corresponding to amorphization of the crystal as discussed below (Fig. 2(b)). Both the 3.1 and 1.9 eV bands were clear from the beginning of the irradiation and their intensities decreased with increasing H^+ fluence. This means that both were due to the intrinsic defects such as $B_{2\beta}$ and NBOHC and were destroyed or turned to some defects with different characters.

Tohmon et al. [6] and Skuja et al. [5] have reported that two oxygen deficiencies related to B_2 band emissions are excited by around 5.1 eV photons, and 2.7 eV emission is attributed to $B_{2\alpha}$ (≡Si:Si≡) and 3.1 eV to $B_{2\beta}$ (O–Si–O). The emission bands attributed to $B_{2\alpha}$ and $B_{2\beta}$ centers were also observed in our previous luminescence measurements of silica glasses under in-reactor irradiation.[2–4] Therefore, the present ion-induced luminescence at 3.1 and 2.7 eV likely originate from the $B_{2\beta}$ center and the $B_{2\alpha}$ center, respectively. However, the variation of the 2.7 eV emission suggests superposing of the emissions with different characters. We will discuss the origin of the 2.7 eV emission in detail.

4.2. Variation of the 2.7 eV emission band in silica glasses

As indicated above, the 2.7 eV emission band likely changed to different character with increasing fluence. The first increase of the band intensity for the glasses was found to obey a linear relationship with irradiation does (dpa), indicating the production of a specific defect assigned to $B_{2\alpha}$ center by the displacement effect of the incident H atoms. The following decrease of the intensity would correspond to the annihilation of $B_{2\alpha}$ centers due to the clustering of defects and/or the formation of Si precipitates, which do not contribute to the emission band. Actually, the FWHM of this band tended to broaden by prolonged irradiation (Fig. 2(d)), indicating the formation of complex defects in silica samples. Our previous XAFS (X-ray absorption fine structure) analyses also revealed that Si precipitates were produced in silica glasses through atomic displacement by neutron irradiation [13], supporting the possibility of Si precipitation by the present H^+ irradiation.

Here, we discuss the second increase of the 2.7 eV band intensity at the fluence ranging $0.5–3\times10^{16}$ H^+/cm^2. In this fluence region, FWHM of the 2.7 eV band increased suddenly (Fig. 2(d)), suggesting the multiple origins of emission centers. In our previous measurements of He^+-induced luminescence of silica glass, the same 2.7 eV emission band was observed, and the band intensity first rapidly increased, and then decreased monotonically to certain intensities without any temporal increase on He^+ irradiation. Therefore, the temporal increase shown in Fig. 2(c) is expected to be related to implanted hydrogen. Our FT-IR analyses showed that implanted hydrogen atoms are retained in the forms of Si–OH and Si–H up to ca. 5×10^{16} H^+/cm^2, and the implanted hydrogen atoms started to form H_2 gaseous molecules around this irradiation dose [14]. In other words, generated Si–H and Si–OH sites must be extracted by subsequently implanting hydrogen to form H_2 molecules, so that the remaining Si- (oxygen vacancy) or Si–O dangling bonds would provide a new emission center. On the other hand, an implantation generated Si–OH site itself could be a new emission center, as the emission band attributed to the Si–OH site was reported to appear in the energy region near 2.7 eV. Thus, the second peak of the band intensity around 2.7 eV likely results from the generation of emission centers related to implanted hydrogen.

Now let us compare the damage processes under H^+ irradiation among the high- and low-OH silica glasses, based on the variation of the intensity and FWHM of the 2.7 eV band. In the early stage of H^+ irradiation, both high- and low-OH silica glasses showed similar rapid increase of intensity, which was assigned to the production of $B_{2\alpha}$ centers through atomic displacements. However, the intensity of this band was always higher for the high-OH silica glass, suggesting that a larger amount of $B_{2\alpha}$ centers are generated in the high-OH silica glass compared with the low-OH silica glass.

The difference between these two types of silica glass was also found in the variation of the FWHM of the 2.7 eV band. In the low-OH silica glass, the appearance of the second peak is very clear together with the minimum of the FWHM at around 1×10^{16} H^+/cm^2, indicating that the first 2.7 eV band was replaced by the second appearing 2.7 eV band with a different character. In the high-OH silica glass, the appearance of the second peak was not as clear as that of the low-OH silica glass, while the increase of FWHM in the high-OH silica is significant over the fluence of 5×10^{16} H^+/cm^2. Therefore the appearance of the second peak was attributed to band broadening or a change to a multi-component band. The high-OH silica glass seems to allow the production of new defects with different characters more than does the low-OH silica glass.

This difference in the 2.7 eV band emission change between high- and low-OH silica glasses must be related to the difference in the amount of intrinsic OH in silica glasses, and very likely can be explained by the

structural analyses using XAFS in our previous study [13,14]. It is known that silica glasses consist of odd- and even-number atomic rings in the Si–O–Si bond networks, ranging over three to eight-member rings, while a silica crystal has a regular ordered structure consisting of only six-member rings [15]. XAFS analyses indicated that the average ring sizes in the silica samples are larger in the following order; silica single crystal < low-OH silica glass < high-OH silica glass [13]. In other words, distortion of the Si–O–Si bond network from the regular ordered one is larger for the high-OH silica glass. It is speculated that the larger the deviation from the regular network structure, the easier for displaced atoms (either or both of oxygen and silicon) to find sites to be stabilized instead of the recombination to the original sites. Actually, our separate FT-IR analyses has indicated that the high-OH silica glass has a tendency to trap more hydrogen in the form of SiO–H or Si–H bonds, compared to the low-OH silica glass [14].

4.3. The variation of the 2.7 eV emission band in silica single crystal

In the silica single crystal, the first peak of the 2.7 eV band appeared in higher fluence, while the height of 2.2 eV peak assigned as the *F* center characteristic to the crystalline decreased with fluence. Taken into account that the fluence for the first increase of the 2.7 eV band, 2×10^{16} H^+/cm^2 (0.05 dpa), corresponds to the threshold dpa for the amorphization of SiO_2 crystals [14], the first appearance of the 2.7 eV band in the crystal is most likely caused by the same origin, i.e. of $B_{2\alpha}$ centers observed in both glasses.

In the crystal, the second peak of 2.7 eV band intensity was significant in the fluence region of 2×10^{17} H^+/cm^2 (Fig. 2(c-3)), with appreciable band sharpening (reduction of FWHM) (Fig. 2(d-3)). This is confirmation of the multiple origins of the 2.7 eV peak as suggested in the glasses. Since the volume or space around lattice atoms in a crystal is smaller than that in a glass, the former even after the amorphization must be smaller than that for the low-OH glass. Accordingly the implanted H can only be stabilized after the amorphization and rather stable OH-related defects appeared after the irradiation to very high fluences. In other words, defect formation (damage) processes after the occurrence of amorphization would be essentially the same as that in the low-OH silica glass. This result may emphasize the effects of intrinsic OH on the damage process of silica samples, because we confirmed that the content of intrinsic OH in the present silica single crystal is the same level as that in low-OH silica glass by FT-IR analyses. However, the above discussion is still speculative, and further work is required. Nevertheless, we can conclude that the detailed investigation of the H^+ induced luminescence from silica gives useful information to understand the dynamic damage processes under H^+ irradiation.

5. Summary

We have performed in-situ analyses of luminescence from silica glass (high-OH and low-OH silica glasses) and a silica single crystal induced by H^+ irradiation to study the damage process in the silica samples. The luminescence spectra of these silica samples induced by H^+ ions showed emission bands centered at around 1.9, 2.2, 2.7 and 3.1 eV, respectively assigned to NBOHC, F center in a crystal, $B_{2\alpha}$ centers and/or SiOH related centers newly produced defects in silica glasses and $B_{2\beta}$ centers.

For the glasses, the intensity of the 2.7 eV band first increased and then gradually decreased, and which were respectively attributed to production of the $B_{2\alpha}$ oxygen deficient centers and their subsequent transformation into other non-luminatinig defects or defect clustering. With increasing H^+ fluence, new OH-related defects with the luminescence centered also at 2.7 eV appeared. It was found that irradiation-induced defects and implanted hydrogen were more stable in the high-OH silica glass owing to its larger open space in silica network structure compared with that of the low-OH silica glass. In the silica single crystal, the amorphization occurred first and then the $B_{2\alpha}$ centers started to grow and changed to the OH-related defects in a similar manner as observed in the glasses. However the appearance of the OH-related defects was more appreciable because of the greater structure restrictions in the amorphized crystal.

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