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Luminescence characteristics and defect formation in silica glasses under H and He ion irradiation

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Abstract

Ion beam induced luminescence from silica glasses containing various OH concentrations was measured to examine the effects of OH and the energy deposition processes on the damage creation under irradiation by H and He ions in the energy range 0.2–3.0 MeV. The 2.7 eV luminescence center corresponding to the $B_{2\alpha}$ oxygen deficiency centers was less effectively created in the high-OH silica, where the 1.9 eV luminescence originating from the non-bridging oxygen hole centers were prominent. Ion implantation and thermal release experiments showed that MeV ion induced defects trapped hydrogen along its trajectory as a form of Si–H. Annihilation of $B_{2\alpha}$ centers can be promoted in high-OH silica, by trapping of hydrogen released by the ion induced dissociation of OH. The energy dependence of the initial growth rate of luminescence suggested that the relatively large electronic energy loss of He ions plays roles in excitation and/or production of oxygen vacancies.
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1. Introduction

Understanding the damage processes in the dielectric materials such as silica under irradiation is important for developing the diagnostic systems used in fusion and fission environments [1,2]. Fundamental defects such as the E′ center, the peroxy radical and non-bridging oxygen hole center (NBOHC) in silica glasses, have been extensively studied by electron paramagnetic resonance (EPR). Besides the defects having an un-pared electron, neutral oxygen deficiency defects (ODCs) are also essential intrinsic defects, which affect optical absorption in practical application [3,4]. Additionally, it is well-known that ODCs interact with atomic hydrogen [5], which is one of the major impurities in silica glass as a form of hydroxyl (OH). The non-paramagnetic B_2 centers are known to emit blue luminescence at around 2.7 eV ($B_{2\alpha}$) and 3.1 eV ($B_{2\beta}$) when irradiated by ionizing radiation [6,7]. Therefore, an ion beam is one of the alternative probes that can be used to detect non-paramagnetic ODCs. The in situ luminescence measurements during ion bombardment are also powerful methods to measure dynamic process involved damage creation and relaxation in the glass [8–10]. For damage processes, not only nuclear collisions but also electronic energy deposition can create Frenkel type defects in silica glasses [11]. Because the observed phenomena is composed of

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complex processes such as defect formation and clustering, affected by small amounts of impurities, ion beam induced luminescence from silica glasses is not clearly understand.

In the present experiment we measured the ion beam induced luminescence in silica glasses with various OH concentration under H and He irradiation in the energy range 0.2–3.0 MeV, to examine the characteristics of the luminescence and to clarify the effects of OH, the nuclear effects, and the electronic energy deposition on the defect formation.

2. Experimental

Samples of SiO_2 glasses studied were commercially available fused and synthesized silica glasses, produced by Toshiba Ceramics, Co. Ltd., with a size of 10 mm × 10 mm and a thickness of 0.5 mm. The nominal concentration of impurities in each sample is tabulated in Table 1, with observed intensity of the 3.1 eV luminescence measured by photo luminescence (PL) experiments, which were carried out using a Xe lamp with a 5 eV interference filter. Ion beam induced luminescence was measured at room temperature using a scattering chamber with base pressure of 2×10^{-6} Pa, connected to a 1.7 MV tandem accelerator at the Institute for Materials Research, Tohoku University. An ion beam of about 1 mm diameter was incident on the specimen at an angle of 40° to the surface normal at energies between 0.2 and 3.0 MeV with a flux density of about 10 nA/mm^2, corresponding to 6×10^{16} ions/m^2 s. The ion induced luminescence was transmitted by optical fibers inserted in the vacuum chamber or by an optical window, and was detected using a monochrometer (ActonResearch SP-2356) equipped with a CCD camera (RoperScientific PIXE100). A low energy ion gun with a velocity filter was also equipped on the chamber to perform the keV energy D^+ ion implantation. Hydrogen concentration in the near surface layer was determined by elastic recoil detection analysis (ERDA). An ion beam of 2.8 MeV He^{2+} was incident on the specimen at an angle of 75° to the surface normal and the recoiled hydrogen atoms were detected at an angle of 30° with respect to the analyzing beam using an Al foil of 12 μm thickness to stop the forward scattered He ions.

3. Results and discussion

Under the H or He irradiation, three characteristic luminescence peaks were observed at 1.9, 2.7 and 3.1 eV [12], depending on the OH content in the silica glasses. A prominent broad peak at 2.7 eV is attributed to oxygen monovacancies, denoted the $B_{2\alpha}$ band [7], and a relatively small peak at 1.9 eV corresponds to the NBOHCs [13]. Luminescence at 3.1 eV was thought to originate from intrinsic ODCs, connected to $B_{2\beta}$ band [7], observed only at very small fluences of ion irradiation on fused silica samples, and immediately diminished and the 2.7 eV luminescence started to increase with successive irradiation [12]. Figs. 1(a) and (b) show fluence dependence of normalized intensity of the luminescence from silica glasses with different OH contents, for the 2.7 eV and 1.9 eV luminescence, respectively. The higher intensity of 2.7 eV luminescence for lower OH silica may be explained by a speculation that the glass network was more strained in low-OH silica, where strained Si–O–Si bonds are easily broken into oxygen deficiency centers to stabilize the glass network [14]. The intensity of the 3.1 eV luminescence by PL experiments was also higher for the low-OH silica as shown in Table 1, indicating that the $B_{2\beta}$ centers can be related to the precursor of the 2.7 eV luminescence center.

The 1.9 eV luminescence increased at the beginning of the irradiation, but immediately saturated for fluences above 2×10^{18} H/m^2. In contrast to the intensity of 2.7 eV luminescence, the intensity of 1.9 eV luminescence was lower for silica glasses with higher OH (Fig. 1(b)). This can be reasonably explained by the formation of NBOHCs in high-OH silica by the ion induced dissociation of OH. Also, this mechanism is expected to be a source of atomic

Table 1
Nominal concentration of impurities, and measured PL intensity of 3.1 eV peak, for silica glasses studied

Sample	Al (wt ppm)	Fe (wt ppm)	Na (wt ppm)	Cu (wt ppm)	OH (wt ppm)	ODCs 3.1 eV (PL) arbitrary units
Fused silica (T-1030)	8	0.3	0.8	0.02	200	300
Fused silica (T-2630)	8	0.3	0.3	0.01	1	500
Synthesized silica (T-4040)	0.021	0.023	0.011	0.001	800	0

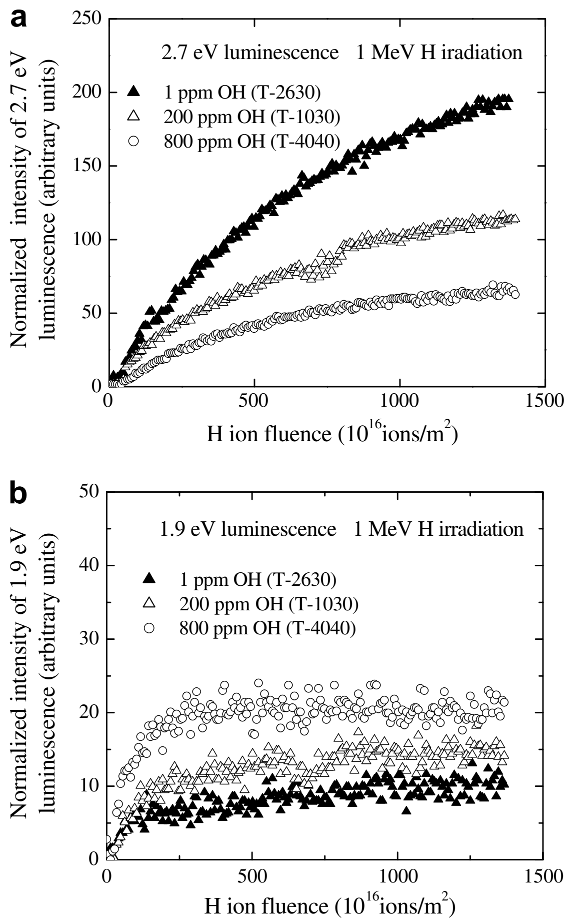


Fig. 1. Normalized intensity of ion induced luminescence from three types of silica glasses with different OH contents plotted against the incident fluence of 1 MeV H ions, for the 2.7 eV and 1.9 eV peaks, (a) and (b), respectively.

hydrogen. For gamma-ray irradiation, enhanced photo-generation of E′ centers was found for H_2 treated oxygen deficient silica [15], in which the mechanism proposed that an oxygen vacancy traps an atomic hydrogen induced by photo ionization and finally transforms to an E′ center. Similarly, the counter part of the NBOHCs formation can supply atomic hydrogen, which can be trapped by an oxygen vacancy, leading to transformation of the oxygen vacancy into the E′ center. The observed low intensity of 2.7 eV luminescence for high-OH silica supports the above speculation about the annihilation of the $B_{2\alpha}$ oxygen deficiency centers by trapping hydrogen created from the ion induced dissociation of OH.

Fig. 2 shows deuterium concentration profiles obtained by the ERDA measurements plotted against the depth in the silica glass (T-1030) during the implantation of 5 keV D ions. After the D ion implantation to a dose about 1×10^{22} D/m^2 at room temperature, the D atoms were trapped only in the near surface layer corresponding to the projected range of the D ion. When 2.8 MeV He ions of the analyzing beam simultaneously bombarded the surface to a fluence of 1×10^{20} ions/m^2 during the 5 keV D ion implantation, a flat distribution of D atoms with a concentration of about 1×10^{17} m^{-3} was observed in the interior of the sample, far beyond the range of the implanted D ion. Because no accumulation of D atoms occurred without the He irradiation, implanted D atoms must have diffused into the interior of the silica and were trapped by damage caused by the He irradiation.

The thermal release behavior of the D atoms retained in the silica glass during isochronal annealing for 10 min at each temperature is shown in Fig. 3. The fused silica (T-1030) was implanted with 5 keV D ions to 3.0×10^{21} D/m^2, and was simultaneously irradiated with 2.8 MeV ^{4}He ions with 1×10^{20} He/m^2. The release of the retained D atoms from the surface occurred in a wide range of the annealing temperature, probably because of complex defects in the D ion implanted depth region. On the other hand, the D atoms uniformly distributed in the interior of in the silica glasses were mainly released at temperatures above 800 K, corresponding to breaking bonds of Si–H [16], indicating

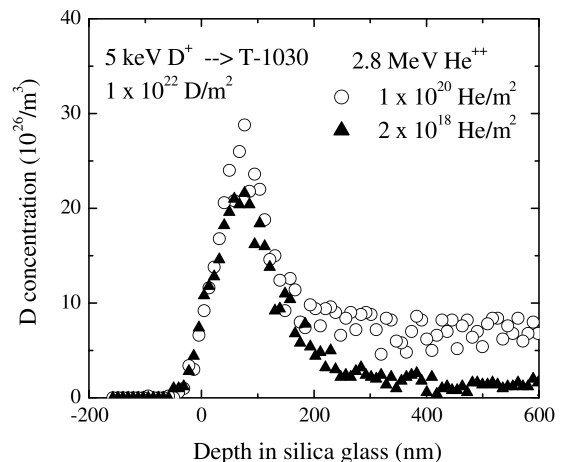


Fig. 2. Concentration depth profiles of D atoms measured by the ERDA measurements for fulsed silica (T-1030) irradiated by 5 keV D ions to a fluence of 1.0×10^{22} D/m^2 at room temperature. The ions of the 2.8 MeV $^4He^{++}$ analyzing beam were simultaneously bombareded to a fluence of 1×10^{20} He/m^2 (○) and 2×10^{18} He/m^2 (▲).

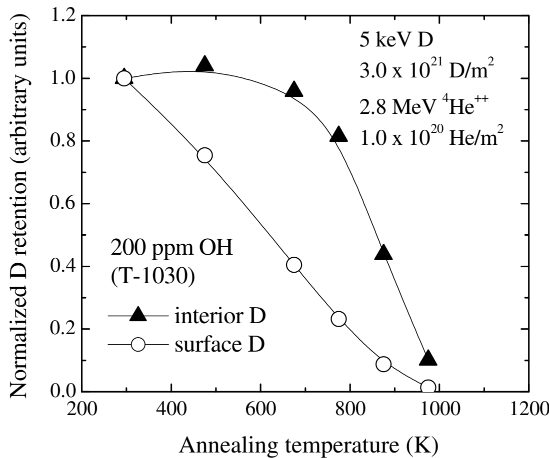


Fig. 3. The retained D fractions in the fused silica (T-1030) implanted by 5 keV D ions to 3.0×10^{21} D/m^2, simultaneously irradiated by 2.8 MeV ^{4}He ions with 1×10^{20} He/m^2, measured after each stage of the isochronal annealing for 10 min. The D retention was normalized to the retention at room temperature.

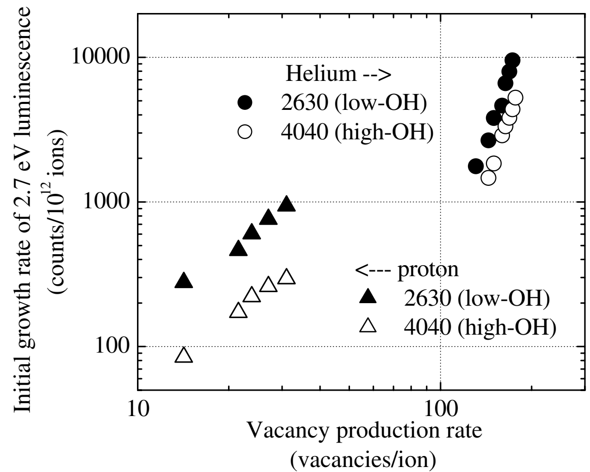
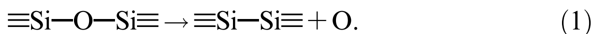


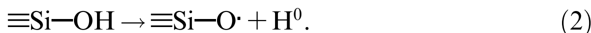
Fig. 4. Initial growth rate of 2.7 eV luminescence from silica glasses with low and high OH contents, plotted against the vacancy production rate calculated using the SRIM2003 [17], for H and He ion irradiation.

that the MeV ion induced defects trap hydrogen along its trajectory as a form of Si–H. According to the result of the 2.7 eV luminescence under H and He irradiation, an oxygen vacancy related with $B_{2\alpha}$ band is created by the ion irradiation



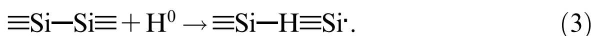
$$\equiv\text{Si—O—Si}\equiv \rightarrow \equiv\text{Si—Si}\equiv + \text{O}. \quad (1)$$

Simultaneously, hydrogen is liberated by the ion induced dissociation of OH



$$\equiv\text{Si—OH} \rightarrow \equiv\text{Si—O}^{\cdot} + \text{H}^0. \quad (2)$$

In fact, the formation of NBOHC was confirmed as an increase of 1.9 eV luminescence in high-OH silica glasses. An E'_β center ($\equiv$Si—H$\equiv$Si$^{\cdot}$) can be formed by diffusion and subsequent trapping of the atomic hydrogen at the site of oxygen vacancy [14]



$$\equiv\text{Si—Si}\equiv + \text{H}^0 \rightarrow \equiv\text{Si—H}\equiv\text{Si}^{\cdot}. \quad (3)$$

This suggests that hydrogen released from OH in silica glasses under ion irradiation plays a role in the conversion of $B_{2\alpha}$ oxygen vacancy into an E'_β center, and contributes to suppress the intensity of ion induced 2.7 eV luminescence.

The production rate of oxygen vacancies responsible for the luminescence can be evaluated from the increase rates of the luminescence at a very low fluence if we assume that (i) the initial concentration of the $B_{2\alpha}$ luminescence centers is negligible, (ii) and initial increase rate of the luminescence depend on the production rate of luminescence centers and their excitation, but not on annihilation of the luminescence centers due to clustering of defects. For various incident ion energies between 0.2 and 3 MeV, growth rates of 2.7 eV luminescence were estimated at low fluences, below 5×10^{18} ions/m^2, and plotted against the rate of vacancy production calculated using the SRIM2003 [17] code based on Kinchin–Pease formalism. Fig. 4 gives the results for the H and He irradiation. It is clearly seen that the initial growth rate of the 2.7 eV luminescence was higher for the low-OH silica glasses by H and He ions irradiation. Extrapolated curves of the plotted data for H and He irradiation do not coincide with each other; the He ion induced growth rate increased more rapidly with increasing the vacancy production rate. In contrast to the present results for MeV energy H and He ion irradiation, a linear relationship between the displacement rate by nuclear collisions and initial increase of ion induced luminescence was reported [8] for the D and He ions below 30 keV. This discrepancy may be attributed to the difference of the electronic excitation process of the ions between keV and MeV energies. For example, the electronic energy loss of D and He ions below 10 keV is comparable, or a little smaller for He ions. Above 0.2 MeV, the electronic energy loss of He, however, is several times larger than that of H ions. Relatively dense electronic excitation of He ions in the present energy region may have influence not only on the excitation of the luminescence centers, but also on the production behavior of oxygen vacancies.

4. Summary

We measured the ion beam induced luminescence from silica glasses under H and He ion irradiation to study the effects of OH on damage creation. The 2.7 eV luminescence centers, corresponding to the $B_{2\alpha}$ oxygen deficiency, were more effectively created in lower OH silica glasses. On the other hand, formation of 1.9 eV luminescence corresponding to NBOHC was prominent for high-OH silica. The MeV He ion induced hydrogen trapping was confirmed and the thermal release behavior of this hydrogen indicated Si–H bond formation. It can be stated that the formation of the $B_{2\alpha}$ centers during the ion irradiation was suppressed by transformation of the oxygen vacancy into non-illuminating bands such as E'_{β} centers due to trapping of the atomic hydrogen originating from ion induced dissociation of OH. The energy dependence of the initial growth rates of 2.7 eV luminescence showed that the excitation and/or production of the luminescence center can be attributed to relatively large electronic energy loss of He ions above 0.2 MeV.

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