



Damage process and luminescent characteristics in silica glasses under ion irradiation

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A B S T R A C T

The formation and annihilation behavior of the oxygen vacancies in silica glasses under 0.1 – 3.0 MeV H and He ion irradiation were studied using ion induced luminescence. Characteristics of the luminescence efficiency by the ion energy deposition were examined using thin SiO₂ films prepared by sputtering followed by thermal oxidation. The ion induced 2.7 eV luminescence linearly increased with increasing the electronic stopping of H ions in the range between 20 and 150 eV nm⁻¹, while it was nearly constant for He ions in the range between 200 and 370 eV nm⁻¹. The evolution curves of the luminescence intensity during the H and He ion irradiation can be explained by the defect production mainly by the nuclear collision and its annihilation by electronic energy deposition.

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1. Introduction

The dynamic irradiation effects on silica glasses are important for developing the diagnostic systems used in fusion and fission environments. Fundamental defects such as the E-centers, the peroxy radical and non-bridging oxygen hole center (NBOHC) in silica glasses, have been extensively studied by electron paramagnetic resonance (EPR). Besides these defects having un-paired electron, neutral oxygen deficiency centers (ODCs) have received considerable attention, because they are also essential defects, which affect optical absorption for practical application [1,2]. Nevertheless, our knowledge about ODCs is still limited because of their diamagnetic characteristic. The ion beam is one of the alternative probes to detect B₂ absorption bands, which corresponds to non-relaxed oxygen vacancy denoted as ODC(II). These non-paramagnetic B₂ centers are known to emit blue luminescence at around 2.7 eV (B_{2α}) and 3.1 eV (B_{2β}) by the ionizing radiation [3,4]. The luminescence measurements during ion bombardment also allow us to measure dynamic process involved damage creation and relaxation in the glass network [5,6] affected by impurities such as OH hydrogen [7,8]. On the other hand, the analysis of the ion induced luminescence in SiO₂ glasses is complicated owing to the simultaneous measurement of damage process and luminescent phenomenon. In the present study, we first examined the characteristics of the ion induced luminescence such as emission efficiency, and then try to analyze damage process quantitatively.

2. Experimental

Samples of SiO₂ glasses used in the present experiments were commercially available synthesized silica glasses (T-4040), produced by Toshiba Ceramics Co. Ltd., with a size of 10 mm × 10 mm with a thickness of 0.5 mm. Nominal concentration of OH was about 800 wt. ppm, and metal impurities such as Al, Fe and Cu were less than 0.3 wt. ppm. To examine the excitation energy dependence of the luminescent centers, thin films (500 nm) of SiO₂ films on Si substrate were prepared by RF magnetron sputtering followed by thermal oxidation in air atmosphere. The film thickness and the elemental composition were examined by Rutherford Backscattering Spectroscopy (RBS).

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 Institute for Materials Research, Tohoku University. An ion beam of about 1 mm diameter was incident on the specimen at the surface normal at energies between 0.1 and 3.0 MeV with a current density of about 10 nA/mm², corresponding to a particle flux density about 6×10^{14} ions/m². The current of the incident ion beam was measured by a retractable Faraday cup in front of the target, and monitored on the target during the irradiation. The observed luminescence yield is exactly proportional to the incident ion flux in the present condition; the luminescence intensity was normalized by the incident current density. The ion induced luminescence was transmitted by optical fibers inserted in the vacuum chamber or by an optical window, and was measured using a monochromator (ActonResearch SP-2356) equipped with a CCD camera (multi-channel spectrum analyzer (RoperScientific PIXE100)). The

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spectrum was analyzed in the wavelengths between 400 and 800 nm, corresponding to the energies between 1.8 and 3.2 eV.

3. Results and discussion

Fig. 1 shows typical ion induced luminescence spectra from thin film SiO₂ and bulk silica glass under 1 MeV He ion bombardment to a fluence of about 2×10^{18} He ions/m² at the room temperature. For both samples, similar broad blue luminescence peaks were observed at around 2.7 eV, and they increased with increasing the He ion fluence at the beginning of the bombardment and tended to saturate from 1×10^{18} He ions/m². According to the RBS measurements, oxygen was uniformly distributed in the whole thickness (500 nm) of the film as SiO_{2,0}, and no other prominent luminescence peak appeared in the energy range between 1.8 and 3.1 eV. A small peak was found at 1.9 eV, which can be attributed to NBOHC, for the synthesized silica glass containing 800 ppm. OH. Anyhow, the identical shapes of the 2.7 eV luminescence for thin film SiO₂ and bulk silica glass indicate that the observed 2.7 eV luminescence was originated from the same luminescence centers.

To measure the ion energy dependence of the 2.7 eV luminescence yield, the sample must contain stable luminescence centers during the measurements. Prior to the measurements, the thin film sample was bombarded by 0.5 MeV H⁺ ion to 2×10^{19} /cm² where the luminescent centers are saturated and uniformly distributed in the 500 nm SiO₂ film. We confirmed that the luminescence intensity did not change before and after the measurements. Fig. 2 shows energy dependence of the intensity of 2.7 eV luminescence from the thin SiO₂ film, where the incident ion energy was varied between 0.1 and 3.0 MeV. The luminescence intensities were evaluated at the peak counts at around 2.7 eV. The ion induced luminescence intensity decreased with increasing the incident energy of H ions, while it was independent of the incident energy of He ions. The incident ions can completely penetrate the SiO₂ film of 500 nm thickness, and the change of the ion energy in the SiO₂ film is relatively small. Thus, the observed luminescence intensity corresponds to the yield of the 2.7 eV luminescence from the luminescence centers per unit length by a certain amount of the electronic excitation caused by incident H and He ion. This excitation characteristic was re-plotted as a function of the electronic energy deposition of the H and He ions into SiO₂ film as shown in Fig. 3. The luminescent efficiency is proportional to the electronic energy deposition for H ions and is independent at higher energy deposition for He ions. This saturation behavior of the deposition energy

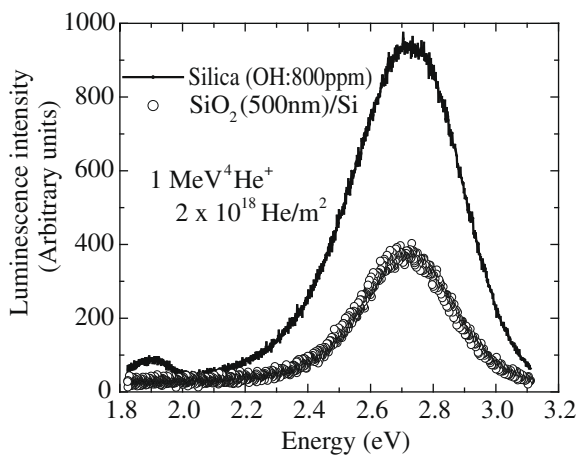


Fig. 1. Ion induced luminescence spectra from SiO₂(500 nm)/Si thin film and silica glass (T-4040: 800 ppm OH) under 1 MeV He irradiation at the fluence of 1×10^{18} He/m².

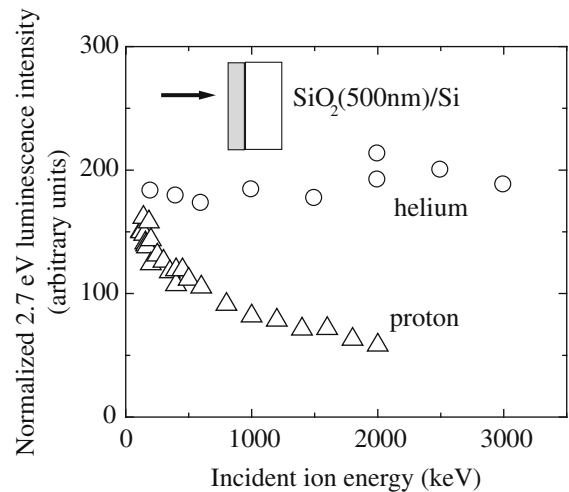


Fig. 2. Normalized intensity of 2.7 eV luminescence of SiO₂(500 nm)/Si plotted as a function of incident ion energy for H(Δ) and He(\circ) ion irradiation.

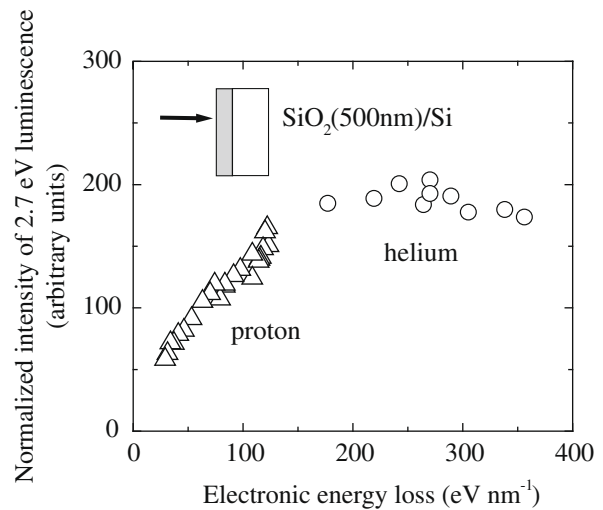


Fig. 3. Normalized intensity of 2.7 eV luminescence of SiO₂(500 nm)/Si plotted as a function of electronic energy loss for H(Δ) and He(\circ) ion irradiation.

dependence for He ion induced luminescence can be attributed to the long lived excited states. Because the 2.7 eV band is thought to be related with the triplet excited states, the decay time of the luminescence is as long as an order of ms [1]. For high density of the energy deposition along the He ion trajectory, the additional energy deposition does not contribute to luminescence while the luminescence centers stay at the excited states.

In an ordinary bulk silica sample, the observed luminescence was integrated along the trajectory of the incident ions, evolving damage process in silica network by ion bombardment. Fig. 4 shows the 1 MeV H and H ion induced luminescence at room temperature plotted as a function of incident ion fluence. For the T-4040 synthesized silica glass, the ion induced luminescence increased from zero with an increase of the ion fluence, and tended to saturate at higher fluence. If we assume that the luminescence center emits a light due to the electronic excitation by the local energy deposition along the ion trajectory, the observed intensity can be written as,

$$I = \int_0^R K(E)N(x)dx, \quad (1)$$

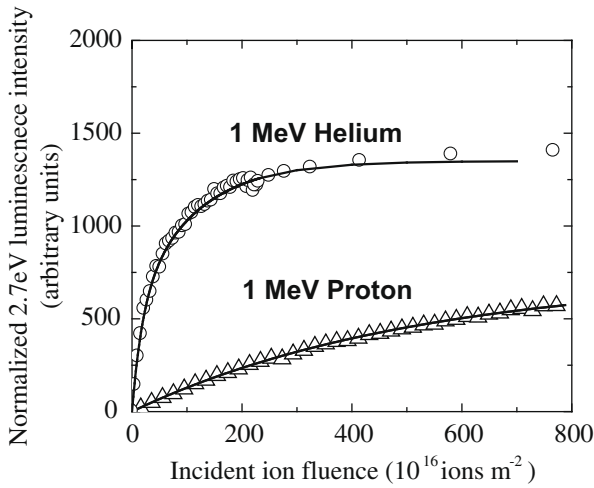


Fig. 4. Evolution of the luminescence intensity under 1 MeV H (○) and He(△) ion irradiation plotted as a function of incident ion fluence. Inserted solid curves are fitted by a model with parameters of production and annihilation rate constants.

where K is the cross-section of creation of the luminescence at energy E of the ion, $N(x)$ is the density of the luminescence centers at depth (x), and R is the projected range of the incident ion. Under 10–20 keV energy H irradiation, the peak position and full width at half maximum (FWHM) of the luminescence spectra influenced at higher fluence probably due to defect clustering [9,10]. In the present energy range 0.1–2 MeV, the peak position and FWHM of the luminescence spectra did not change during the H and He ion irradiation, although the intensity depends on the ion energy and on the fluence. It is reasonable that we assume a type of a luminescence center which is created and annihilated during the H and He ion irradiation. If the formation of a luminescence center is related with one type of oxygen vacancy from the lattice oxygen and annihilation of the luminescence centers is subjected to a first order reaction of them,

$$\frac{dN(x, t)}{dt} = pN_0 - \lambda N(x, t), \quad (2)$$

where p is the production rate of luminescence center, N_0 is density of the oxygen, and λ is the annihilation rate of luminescence center. A solution is derived as

$$N(x, t) = N_0 \frac{p}{\lambda} [1 - \exp(-\lambda \cdot t)]. \quad (3)$$

Well fitted curves were obtained by changing the creation and annihilation parameter p and λ , as inserted in Fig. 4. By evaluating the experimental evolution curve for various incident energies of H and He ion irradiation, the energy dependence of the obtained production and annihilation rate constant were obtained as shown in Fig. 5. Both production and annihilation parameter slightly decreased with increasing the incident ion energy. It can be noticed that the relation between the annihilation and production rates are different for H and He ions. The production rates are higher than the annihilation rate constant for He irradiation. The production rates by H ion irradiation, however, are lower than the annihilation rates especially at higher ion energies, indicating that the annihilation by H ion irradiation is more prominent in comparison with He ion irradiation. Fig. 6 shows the ratio of production and annihilation rate constants of He ion irradiation to that of H ion irradiation, in comparison with the ratio of the nuclear and electronic stopping of He to that of H. The ratio of production rate $P_{\text{He}}/P_{\text{H}}$ is higher than that of annihilation ratio $\lambda_{\text{He}}/\lambda_{\text{H}}$. A similar relation was found between the nuclear stopping ratio $S_{\text{He}}/S_{\text{H}}$ and electronic stopping ratio $Se_{\text{He}}/Se_{\text{H}}$ calculated by SRIM [11], in-

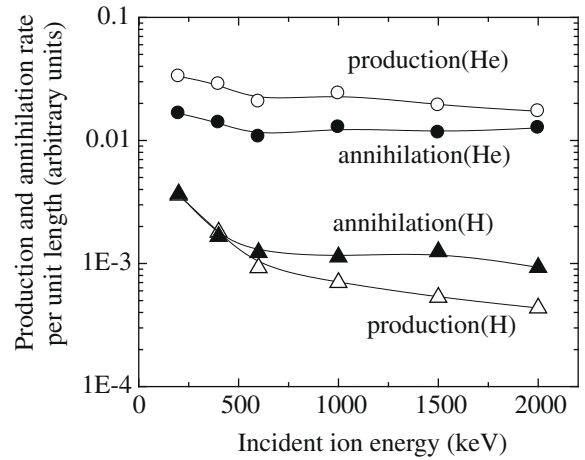


Fig. 5. Production and annihilation rate constants evaluated by a least square fitting for various energy of H and He ions, plotted as a function of the ion energy.

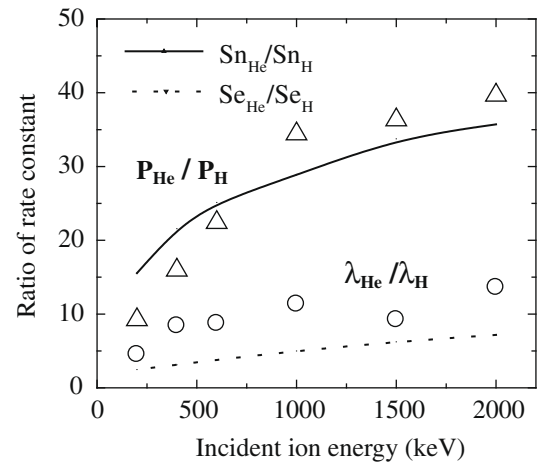


Fig. 6. Ratio of production rate constants of He to that of H ($P_{\text{He}}/P_{\text{H}}$: △) and ratio of annihilation rate constants of He to that of H ($\lambda_{\text{He}}/\lambda_{\text{H}}$: ○), plotted as a function of incident ion energy. Solid curve is ratio of nuclear stopping of He to that of H ($S_{\text{He}}/S_{\text{H}}$). Dashed line is ratio of electronic stopping of He to that of H ($Se_{\text{He}}/Se_{\text{H}}$).

serted in Fig. 6. The production of luminescence centers by He ion irradiation is more effective than that by H ion irradiation, because of higher nuclear stopping for He irradiation. On the contrary, the annihilation by He irradiation is less effective in comparison with the H irradiation, due to relatively lower electronic stopping. This suggests that the annihilation of the ion induced luminescence centers is related to the electronic energy deposition.

4. Summary

Ion induced luminescent characteristics and damage process in thermally oxidized SiO_2 thin film and silica glasses were studied under 0.1–3.0 MeV H and He ion irradiation. The H ion induced 2.7 eV luminescent intensity linearly increased with increasing the electronic stopping of H ion when the SiO_2 film contained a fixed number of luminescence centers. The He ion induced luminescence, however, was independent of the electronic stopping of He ion. The energy independent characteristic of the He induced luminescence by higher electronic energy deposition can be related with the long decay time of the 2.7 eV excitation state. The analysis of the evolution curves of the ion induced 2.7 eV

luminescence intensity indicates that the production of the oxygen vacancies is mainly attributed to the nuclear collisions, and the annihilation of them is caused by annealing effects due to the electronic energy deposition.

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