



Dynamic effects in energetic particle-induced luminescence of SiO₂

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Abstract

Dynamical measurements of ion-induced luminescence and *in-reactor* luminescence of SiO₂ glass have been performed. First the dynamic effects of the ion-induced luminescence are compared between D⁺ and He⁺ ion irradiations, and then the time evolution of the *in-reactor* luminescence change with neutron fluence is compared with that observed in the ion-induced luminescence. Finally, the origin of the luminescence center is discussed. The luminescence spectra of silica glasses induced by D⁺ and He⁺ irradiation have been found to be very similar to cathodoluminescence originating from the centers associated with oxygen vacancies, and the intensity is proportional to the deposited energy by electron excitation irrespective of the incident ion species. The luminescence intensity changes with ion fluence, first increasing, then reaching a maximum and finally decreasing to the nearly steady value after prolonged irradiation. When the fluence is converted to displacement per atom (dpa) value, changes of the luminescence intensity under D⁺ and He⁺ irradiations are very similar. From dynamical change of the luminescence intensity, the first increase of the luminescence intensity is attributed to the increase of newly produced point defects or to an oxygen deficiency due to atomic displacement. The observed decrease is attributed to the association of the point defects, for example, formation of segregated Si or more complex defects. In-reactor luminescence also reveals an intensity increase caused by neutron-induced displacement. The present work clearly demonstrates that dynamic measurement of the ion-induced luminescence can give detailed information on the processes of defect formation in optically transparent materials. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Dynamic effects of neutron irradiation in ceramics have been observed as radiation-induced electrical degradation (RIED) and/or radiation-induced conductivity (RIC) during in-reactor irradiation [1]. Such dynamic irradiation effects on electrical properties of the ceramics must correlate with an electron excitation and hence with optical properties. Comparing with electron irradiation, the dynamic effects of ion irradiation and neutron irradiation have not been extensively examined well

and are therefore one of the main concerns for the application of insulators in fusion devices.

In our previous work we have made a systematic study of ion-induced luminescence of silica (SiO₂) glass to obtain reliable time-averaged spectra free from instabilities due to the charge-up of the specimen with the aid of multichannel analyzer [2,3]. Consequently we have, for the first time, clearly shown that the ion-induced luminescence of SiO₂ is caused by electron excitation by the incident ion with defects produced by the displacement of target atoms performing as additional luminescence centers [2].

Typical defect centers created in SiO₂ glasses by the ion bombardment are oxygen deficiencies which trap one or two electrons referred to as E₁' or E₁'' centers, respectively [4,5]. However, many authors have pointed

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out that the mechanism of luminescence center creation in low-OH concentration SiO_2 is different from that in high-OH SiO_2 and the effect of OH on the luminescence is still an open question [6–8].

In the present work we have conducted dynamical measurements of ion-induced luminescence and in-reactor luminescence of SiO_2 glass, using the nuclear reactor YAYOI at the University of Tokyo. First, the dynamic effects of the ion-induced luminescence are compared between D^+ and He^+ ion irradiations, and then the time evolution of the in-reactor luminescence change with neutron fluence is compared to that observed for the ion-induced luminescence. Finally, the origin of the luminescence centers is discussed.

2. Experimental

Ion-induced luminescence measurements were carried out in a conventional stainless steel vacuum chamber equipped with an ion source and optical spectrometer. D^+ and He^+ ions accelerated up to 30 keV and mass analyzed were injected to an SiO_2 target at ambient temperature (slightly higher than RT due to beam heating) through an aperture of 5 mm in diameter with an incident angle of 45° with respect to the target normal. The injected ion flux was monitored with a Faraday cup in front of the target and a flux of 4.0×10^{14} ions/cm² s was used for the measurement. Because the target ion current could not be measured due to the insulation, implanted fluence was estimated from the irradiation time multiplied by the flux. The vacuum of the chamber during the irradiation was maintained below 1×10^{-6} Pa. The ion-induced luminescence was focused into a visible spectrometer (Spectro Pro 275) whose optical axis was normal to the ion beam and 45° to the target normal through a sapphire window. The photon intensity was detected with a multi-channel analyzer (OMAIH). Details of the experimental setup have been presented elsewhere [2,3].

In-reactor luminescence measurements were made in the nuclear reactor YAYOI at the University of Tokyo. Luminescence from a silica glass (SiO_2) irradiated in the reactor core was transmitted to a spectrometer remote from the core, by a light-guiding tube. During the measurements YAYOI was operated at a maximum power of 500 W, where the neutron flux in the reactor core was about 2×10^{11} n/cm² s with an average neutron energy of 1.3 MeV and the γ -ray level was about 3.0 kGy/h (0.3 MR/h). Thus the radiation effect of γ -rays was superposed on the neutron irradiation effect. Detail of in-reactor luminescence measurement have been presented elsewhere. [9,10].

The specimen used was a synthesized silica (T-4040) disc (13 mm in diameter and 1 mm thick) produced by

Toshiba Ceramics, Japan with nominal OH content of about 800 ppm.

3. Results and discussion

Fig. 1 shows observed luminescence spectra of the synthesized silica after prolonged irradiation of (a) 20 keV- D^+ and (b) 20 keV- He^+ . Both spectra show nearly the same structure, with a broad band centered at 450 nm which is very similar to a cathodoluminescence spectrum given by Mogul et al. [11]. Very similar ion-induced luminescence spectra were also observed by Mogul et al. [11] and Wang et al. [12]. All authors attributed this band to oxygen deficiency trapping two electrons, referred as to the E'_1 center. The intensity of the spectra, however, changed with the fluence as shown in Fig. 2. According to the figure, the intensity changes with time or fluence for D^+ and He^+ were very similar when the fluence was converted to displacement per atom (dpa) by the TRIM code assuming the Kinchin–

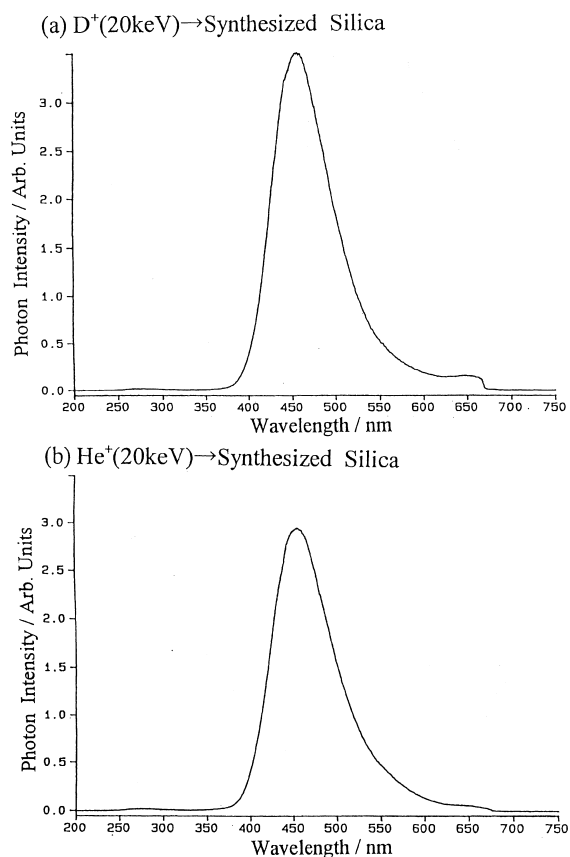


Fig. 1. Observed ion-induced luminescence spectra of synthesized SiO_2 glass after prolonged irradiation of (a) 20 keV D^+ ions and (b) 20 keV He^+ ions.

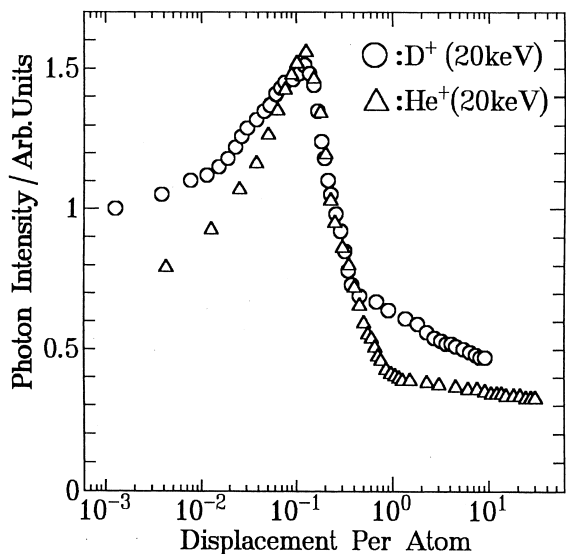


Fig. 2. Changes of luminescence intensity with dpa.

Pease model [13]. With increasing dpa, the intensity first increased to a maximum and then gradually decreased. Above about 1 dpa the intensity stayed nearly constant. The initial intensity increases were found to obey a linear relationship with irradiation time (dpa). Using the least squares fitting algorithm, we get the slopes which are equivalent to production rate coefficients of the luminescence centers and are plotted in Fig. 3 for different ion incident energies. The resulting linear relationship

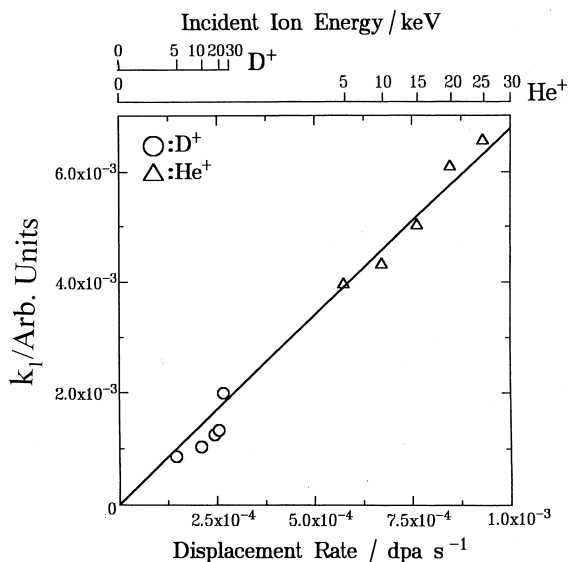


Fig. 3. First order rate coefficient (k_1) of luminescence intensity increase plotted against dpa rate for various incident energies of D and He injection.

confirms that the origin of the luminescence is point defects assigned as oxygen deficiency.

Such a linear increase with the irradiation time is also observed in in-reactor luminescence measurements, as shown in Fig. 4. Since the reactor was operated at different power levels, the intensity was normalized taking neutron flux to be proportional to the reactor power, and plotted against the neutron fluence. Although the luminescence is likely caused by γ radiation, the linear increase of its intensity with the neutron fluence indicates that the luminescence centers are created by the displacement effect of the neutron irradiation.

Thus the initial increase of the luminescence is attributed to the increase in number of point defects associated with oxygen deficiency resulted from the displacement effect of the incident particle, irrespective of the kind of the incident particles.

It is interesting to note that there is almost no difference in the luminescence decay between D^+ and He^+ injections as seen in Fig. 2. The decay was found to be approximated by the square of the time (dpa), indicating second-order decay kinetics. Thus determined second-order rate coefficients of the luminescence decay are plotted against the dpa rate in Fig. 5. It is rather surprising that a very good linear relationship between the rate coefficient and the dpa rate appears again. Considering that this decay appeared after a certain dpa where a large number of point defects must have been produced, the luminescence decay, i.e. the annihilation of the oxygen deficiency, can be attributed to the association of point defects (perhaps clustering of point defects like Si aggregation and/or formation of oxygen bubbles) which do not contribute to the luminescence.

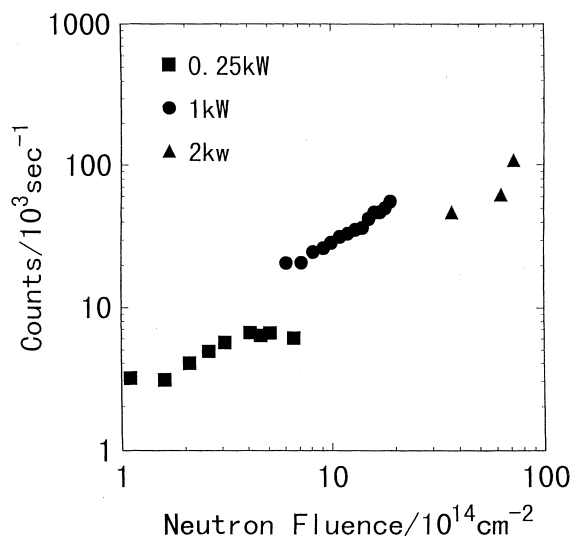


Fig. 4. In-reactor luminescence intensity plotted against neutron fluence.

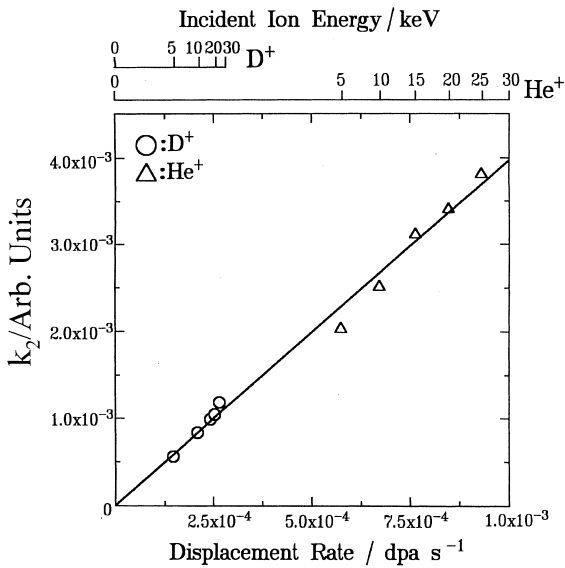


Fig. 5. Second-order rate coefficient (k_2) of intensity decay plotted against dpa rate for various incident energies of D^+ and He^+ injection.

The formation of complex defects is clearly indicated by the change of the FWHM of the luminescence peak when plotted against the dpa, as shown in Fig. 6. One can see that the FWHM monotonically increases with the dpa, suggesting multiple origins of the luminescence centers. Here again the broadening is dependent only on the dpa and irrespective of the incident species.

After prolonged irradiation, the color of the SiO_2 target turned slightly gray. By optical transparency

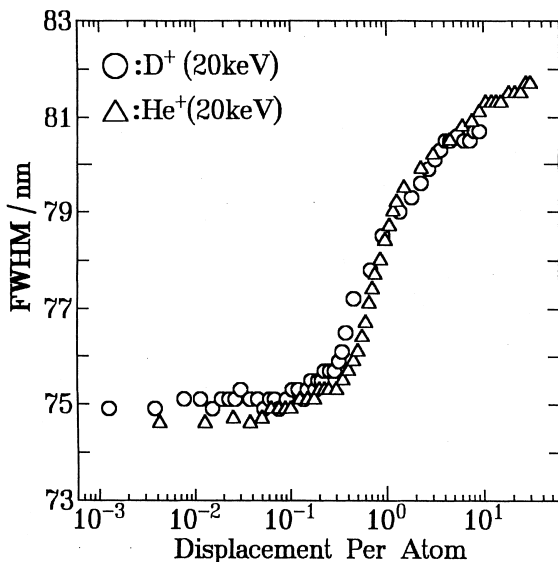


Fig. 6. Change of FWHM of emission band with dpa.

measurements, the irradiated target showed a rather homogeneous reduction of transmittance in the visible wavelength region without appreciable absorption peaks. This suggests the production of local opaque regions or opaque channels, probably owing to the precipitation of Si in the damaged region [14].

Concerning the origin of the luminescence center which has been assigned to the oxygen deficiency, an important question still remains. In the previous work [2] we have clearly shown that the luminescence intensity is strongly correlated with the initial OH content in SiO_2 glasses. In the present work, however, no difference between D^+ and He^+ irradiation was observed. The luminescence intensities are proportional to total deposited energy by electron excitation and increases only with dpa without any influence of implanted D atoms. Therefore, it is important to know the existing state of the implanted D in SiO_2 .

In metals and semiconductors such as Ni, Si and graphite, implanted hydrogen migrates to defect traps produced by the dpa effect [15]. If this is also true in SiO_2 , implanted D should be easily trapped by the created defects, because the number of atoms displaced by the incident ion is larger than that of implanted ions. Consequently the luminescence induced by D^+ irradiation should be more intense than that by He^+ irradiation, in analogy to the increment of the intensity with OH content. This contradicts the present observations. One possible explanation is that the implanted D does not directly bond to oxygen to produce OD but rather bonds to Si or recombines to form D_2 molecules.

Our previous ESR study of D^+ and He^+ irradiated SiO_2 [16] has shown that implanted D atoms very likely prevent an interstitial oxygen atom from recombining with an oxygen vacancy, by occupying dangling bonds of the Si atom neighboring the oxygen vacancy. Since the number of implanted D ions is much smaller than that of the displaced atom as mentioned above, the production of D–Si pairs would have little influence on the total number of oxygen vacancies.

As is well known, silica glass does not inhibit the migration or diffusion of H_2 and He owing to its large open space. The recombination of deuterium to D_2 is very likely, because desorption or accumulation of D_2O would significantly change the chemical composition for the D^+ irradiation. So that the luminescence spectra of D^+ should be different from those of He^+ . The above discussion is still speculative, and further work is needed to clarify the existing state of the implanted D in SiO_2 .

4. Conclusions

We have performed in situ analyses of ion-induced luminescence of silica glasses under D and He ion irradiation by varying incident ion energy and fluence, to

investigate the mechanism and/or origin of the luminescence and the influence of the implanted hydrogen and helium. In-reactor luminescence measurements were also conducted.

The luminescence spectra of synthesized silica glasses induced by D^+ and He^+ irradiation showed a broad band centered at around 450 nm, which is very similar to the cathodoluminescence assigned to oxygen vacancy-related color centers (E'' centers). The luminescence intensity is proportional to the deposited energy by electron excitation in the target irrespective of the incident energy. The luminescence intensity changed with ion fluence, first increasing, then reaching a maximum, and finally decreasing to a nearly steady-state value after prolonged irradiation. When the fluence is converted to dpa, changes of the luminescence intensity under D^+ and He^+ irradiations are very similar. From dynamical change of the luminescence intensity, the first increase of the intensity is attributed to the increase of newly produced point defects by atomic displacement while the decrease is attributed to the clustering of the point defects, e.g. production of oxygen bubbles and Si segregation or more complex defects. In-reactor luminescence also showed an increase caused by neutron-induced displacements.

At the present time we cannot come to clear conclusion as to the assignment of the luminescence centers which have been attributed to oxygen deficiency, but OH has a certain role. In the present work we could not determine the quantum photon yield, the lack of which does not allow us to make a qualitative estimation of the oxygen deficiency production rate per incident ion. Nevertheless this work demonstrates that dynamic measurement of the ion induced luminescence can give detailed information on the process of defect formation in optically transparent materials such as ceramic insulators.

Acknowledgements

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