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Articles

Radiation exposure effect on deuterium retention in SiC

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Heavy ion (Fe^{3+}) irradiation or gamma-ray irradiation of silicon carbide (β-SiC) was done to evaluate the radiation effect on hydrogen isotope retention in SiC. Thereafter, 1 keV D_2^+ implantation or D_2 gas exposure was performed, and their D retentions were evaluated by thermal desorption spectroscopy (TDS). The D_2 TDS spectra consisted of two desorption stages, namely the desorption of D bound to Si as the Si-D bond and C as the C-D bond. The D retention for Fe^{3+} irradiated SiC at the lowest D_2^+ fluence of 0.1×10^{22} D^+ m^{-2} was lower than that for unirradiated SiC. It was expected that the displaced C atoms would be accumulated near the surface region by Fe^{3+} irradiation, leading to their dynamic desorption in methane molecules. For gamma-ray irradiation, C or Si with dangling bonds were formed, which enhanced D trapping. It was concluded that the collision process caused during Fe^{3+} irradiation induced the dissociation of SiC matrix and C aggregates near the surface region, but the electron excitation by gamma-ray irradiation dissociated the single Si-C bond and the quick D trapping by dangling bonds enhanced D retention in SiC.

1. Introduction

Silicon carbide (SiC), in the form of SiC/SiC composites, is being considered for use in the blanket modules for the high temperature gas-cooling system in D-T fusion reactors [1-3]. During D-T fusion operation, SiC would be exposed to severe radiation conditions by neutrons and gamma-rays from transmuted materials. These forms of radiation induce various types of damages by a collision process and an electron excitation process, leading to the retention enhancement of hydrogen isotopes including tritium. In previous studies by the authors [4-6], hydrogen isotope behavior in SiC was extensively studied and it was found that deuterium was preferentially trapped by C and, after saturation of the C-D bond formation, it was trapped by Si in SiC. The deuterium desorption was found to consist of two desorption stages, namely first, desorption of deuterium bound to Si and then, desorption of deuterium bound to C. The trapping mechanisms of the two stages were influenced by the damage structures produced by the D_2^+ implantation. In addition, the deuterium retention in SiC at temperatures above 700 K was higher than that in graphite, where the retention is defined as the area concentration (in the unit of D m^{-2}) of D atoms trapped in material, indicating that tritium retention in SiC may be high.

In ceramics like SiC, two fundamental mechanisms, a cascade collision process and an electron excitation process, are thought to introduce the damage caused by 14 MeV neutrons by DT fusion reaction and energetically exchange charged particles in the SiC [7]. In the fusion environment, both processes will induce irradiation damage in SiC. To elucidate the D trapping mechanism for SiC, it is quite important to separate these two processes. With gamma-ray irradiation, only the electron excitation will be induced. Therefore, the comparison of D retention behavior for heavy-ion irradiated tungsten (W) and gamma-ray irradiated SiC is used quite often. These facts motivated the authors to explore deuterium retention behavior in radiation damaged SiC.

In this study, Fe^{3+} irradiation was done to simulate the cascade collision by neutron irradiation of SiC to avoid the activation of SiC by nuclear reactions induced with neutron irradiation. The gamma-ray irradiation was also done using the cobalt-60 gamma-ray irradiation facility at Shizuoka University. Deuterium retention behavior for damaged SiC was discussed based on the identified damage introduction process.

2. Experimental

Disk-shaped polycrystalline β-SiC (10 mm in diameter and ca. 0.5 mm in thickness) was purchased from Asahi Glass Co. Ltd. and used as sample material. After annealing at 1173 K, 6.4 MeV Fe^{3+} irradiation with a damage level of 0.2 displacement per atom (dpa) was carried out at room temperature using the tandem accelerator at the Dual-Beam Facility for Energy Science and Technology (DuET) in Kyoto University [8-9]. The implantation depth of Fe^{3+} was about 2.3 µm. Cobalt-60 gamma-ray irradiation was performed for other samples at the dose of 100 or 400 kGy at Shizuoka University. After Fe^{3+} irradiation or gamma-ray irradiation, 1 keV D_2^+ was implanted with a flux of 1.0×10^{18} D^+ m^{-2} s^{-1} up to a fluence of 1.0×10^{22} D^+ m^{-2} at room temperature at triple ion implantation system [10]. The implantation depth was 14 nm, which was less than the implantation depth of Fe^{3+}.

The XPS analysis was performed to evaluate the chemical states of SiC using the ESCA1600 system (ULVAC-PHI Inc., Chigasaki, Japan) equipped with an Mg-kα X-ray source (1253.6 eV) and a hemispherical electron analyzer. In addition, a D_2 gas exposure experiment was also performed at 100 kPa for 20 hours at room temperature. The D retention was evaluated by thermal desorption spectroscopy (TDS), with the

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*Corresponding author. E-mail: oya.yasuhisa@shizuoka.ac.jp heating rate of 0.5 K s^{-1} up to 1273 K. The desorbed species were analyzed by a quadruple mass spectrometer (MKS Microvision Plus), whose sensitivity was calibrated using the D_2 standard leak.

3. Results and discussion

Figure 1 shows D_2 TDS spectra for unirradiated SiC and Fe^{3+} irradiated SiC. D_2 desorption consisted of two stages occurring at 890 K and 1080 K. These were attributed to the desorption of D bound to Si as a Si-D bond and that bound to C as a C-D bond, respectively. For unirradiated SiC, after saturation of the C-D bond formation at 1080 K as described previously [4], the Si-D bond became a major trapping state in SiC. However, by Fe^{3+} irradiation, the retentions of D as Si-D and C-D bonds decreased together even at the D^+ fluence of 0.1×10^{22} D^+ m^{-2}. For the fluence of 1.0×10^{22} D^+ m^{-2}, the extent of desorption of D trapped by Si as Si-D bonds was almost equivalent to that for unirradiated SiC.

Total D retention and retentions of D as Si-D and C-D bonds as a function of D^+ fluence are summarized in Figure 2. At the D^+ fluence of 0.1×10^{22} D^+ m^{-2}, total D retention for Fe^{3+} irradiated SiC was half that for unirradiated SiC. The retention of D bound to C as the C-D bond for unirradiated SiC was constant. However, for the Fe^{3+} irradiation case, the D retention increased as the D^+ fluence increased. At the fluence of 1.0×10^{22} D^+ m^{-2}, total D retention was the same as that for that for unirradiated SiC. To evaluate the chemical interaction with D, C 1s XPS analysis was performed as a function of D^+ fluence and the results are shown in Figure 3. Before D_2^+ implantation, two major chemical moieties were found, namely the C-O bond with the binding energy of 286.5 eV and the C-C bond with the binding energy of 284.5 eV. The formation of the C-O bond would be caused by exposure to air after Fe^{3+} irradiation. The existence of the C-C bond would indicate that Fe^{3+} irradiation induced the dissociation of the Si-C bond by the collision process and C was aggregated near the surface region. This fact indicated that Si was dispersed in the SiC matrix, which would induce the D trapping by Si even in the initial stage of D_2^+ implantation. After the D_2^+ implantation, the negative peak shift of the C 1s XPS spectrum was found to be due to chemical sputtering of surface C by the formation of hydrocarbons and the full width at half maximum was increased due to the co-existence of C-D and C-Si bonds. These behaviors were almost in agreement with the TDS results as shown in Figure 1.

To compare the D retention behavior for Fe^{3+} irradiated SiC with that for gamma-ray irradiated SiC, 100 kGy or 400 kGy gamma-ray irradiation was performed. 1 keV D_2^+ was implanted with three fluences of 0.1×10^{22}, 0.5×10^{22} and 1.0×10^{22} D^+ m^{-2} at room temperature. Figure 4 shows D_2 TDS spectra for 100 kGy or 400 kGy gamma-ray irradiated SiC. In

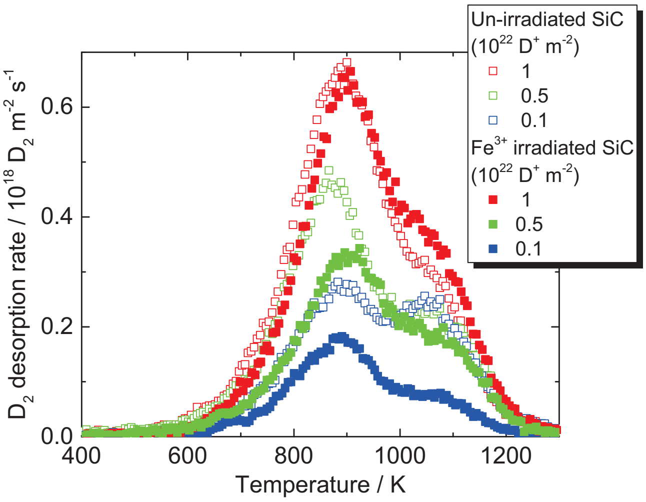

Figure 1. D_2 TDS spectra for unirradiated SiC and Fe^{3+} irradiated SiC as a function of D^+ fluence.

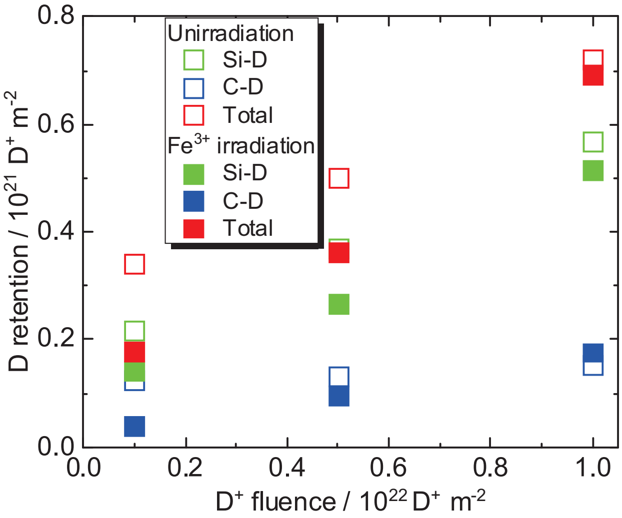

Figure 2. D retention for unirradiated SiC and Fe^{3+} irradiated SiC as a function of D^+ fluence.

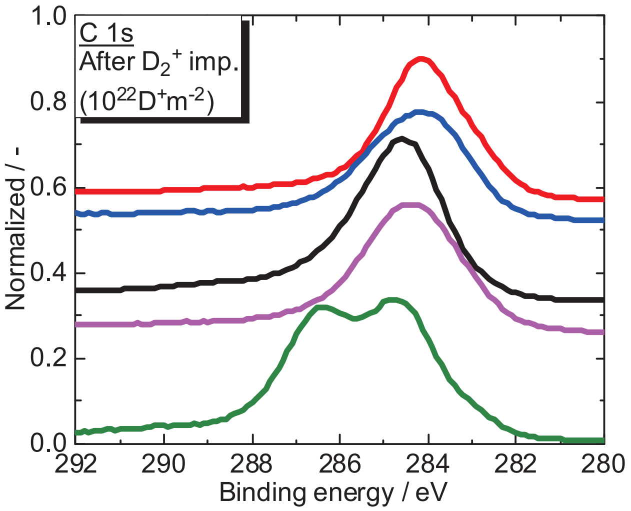

Figure 3. C 1s XPS spectra for Fe^{3+} irradiated SiC as a function of D^+ fluence.

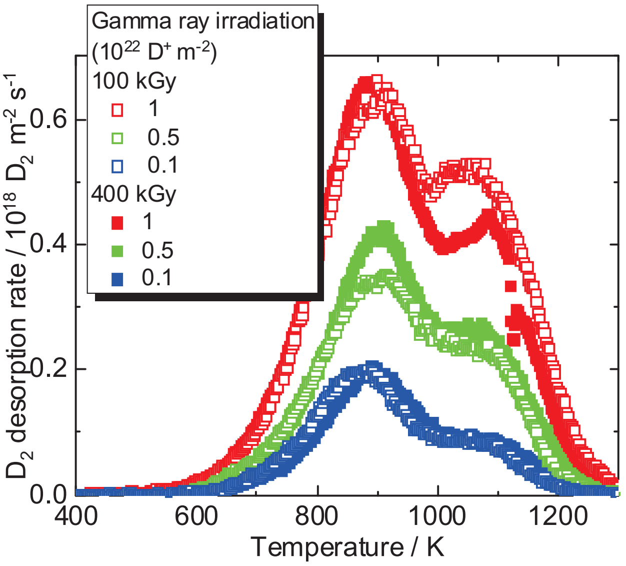

Figure 4. D_2 TDS spectra for 100 kGy or 400 kGy gamma-ray irradiated SiC as a function of D^+ fluence.

the case of the lowest D^+ fluence, 0.1×10^{22} D^+ m^{-2}, it was clear that the shape of the TDS spectra and the extent of the D retention were almost the same as those for Fe^{3+} irradiated SiC. However, two clear desorption stages were found at the highest D^+ fluence of 1.0×10^{22} D^+ m^{-2} for both gamma-ray irradiation cases. Their D retentions are summarized in Figure 5 as a function of D^+ fluence. Large enhancement for the retention of D as the C-D bond was found at 1.0×10^{22} D^+ m^{-2}, although D retention as the Si-D bond was almost directly proportional to the D^+ fluence. C 1s XPS spectra for 400 kGy gamma-ray irradiated SiC as a function of D^+ fluence are shown in Figure 6. Major chemical states of C were assigned as C-Si (282.5 eV) and C-C bonds [11]. It is known that the accumulation of D induces the positive peak shift of C 1s XPS spectra from 284 to 285 eV. After D_2^+ implantation, peak intensity for the C-C bond sharply decreased and the highest peak was shifted toward the higher binding energy side due to formation of the C-D bond; the binding energy reached 284 eV. After the TDS measurement, the peak had largely shifted toward the lower binding energy side due to D desorption, but the C-C bond still existed. This might be caused by some of the C with a dangling bond remaining in the SiC bulk and emerging on the surface due to heating.

To evaluate dynamic trapping by the formation of damage structures by gamma-ray irradiation, 88 kGy gamma-ray irradiation was performed under the D_2 gas exposure condition (in-situ) and their trapping behavior was compared with D_2 gas exposed SiC after gamma-ray irradiation (ex-situ). D_2 gas exposure conditions were the same for in-situ and ex-situ: 100 kPa for 20 hours at room temperature. Figure 7 shows D_2 TDS spectra for in-situ D_2 gas exposed SiC and ex-situ D_2 gas exposed SiC. The spectrum for D_2 gas exposed SiC without gamma-ray irradiation is also shown in this figure. The D_2 desorption was concentrated on the lower temperature side, indicating that D was accumulated near the surface region with a lower trapping energy. Much D desorption was found at temperatures between 600 and 800 K and the D desorption was larger for in-situ D_2 gas exposed SiC than ex-situ D_2 gas exposed SiC, indicating that rapid D trapping by the damage structures produced by gamma-ray irradiation was proceeding. In addition, in Figure 7, no D trapping for SiC without gamma-ray irradiation was found. The D desorption at low temperature would be caused by the adsorption of D at the surface with low trapping energy. From Figure 8, it was clear that D retention was almost doubled compared with that for ex-situ D_2 gas exposed SiC. From these results, it can be concluded that the co-existence of radiation and hydrogen isotopes like fusion environment would enhance D trapping in SiC.

Based on these experimental results, D trapping behavior in SiC is discussed. With Fe^{3+} irradiation, dissociation of the

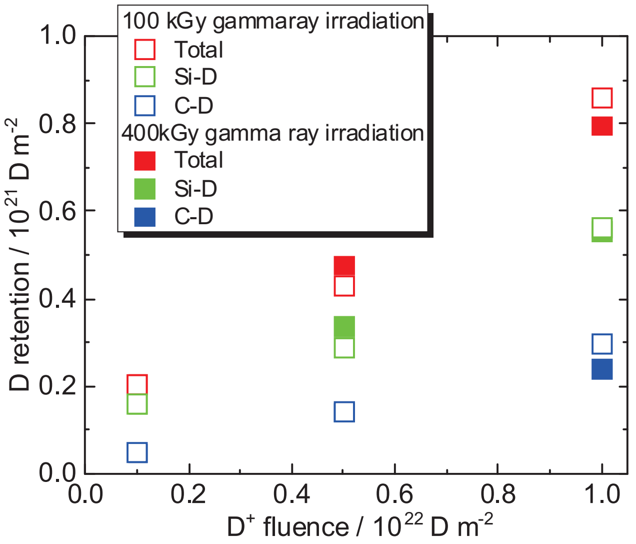

Figure 5. D retention for gamma-ray irradiated SiC with the dose of 100 kGy or 400 kGy as a function of D^+ fluence.

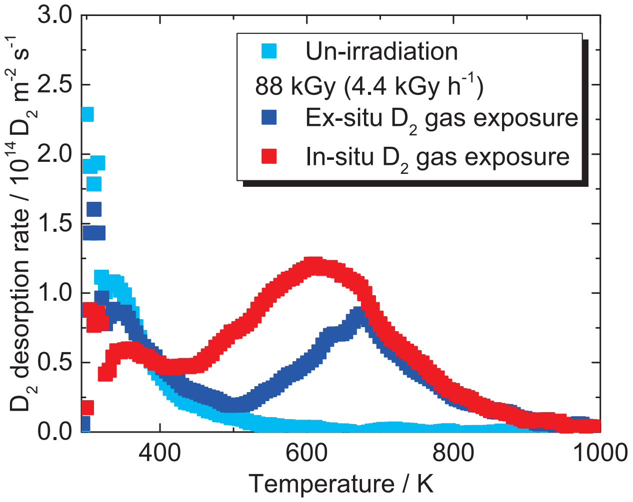

Figure 7. D_2 TDS spectra for D_2 gas exposed SiC during gamma-ray irradiation (in-situ) and after gamma-ray irradiation (ex-situ).

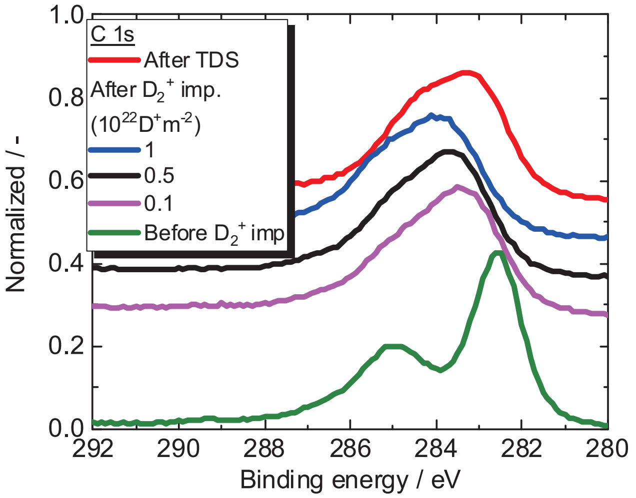

Figure 6. C 1s XPS spectra for 400 kGy gamma-ray irradiated SiC as a function of D^+ fluence.

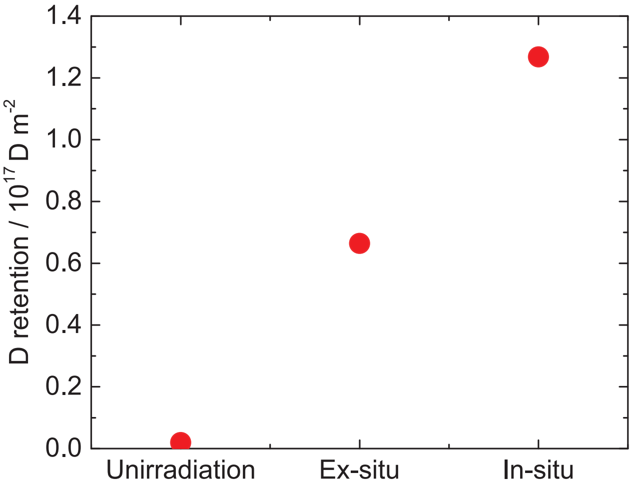

Figure 8. Comparison of D retentions for D_2 gas exposed SiC without gamma-ray irradiation or, ex-situ or in-situ gamma-ray irradiation.

Si-C bond was induced, especially near the surface region, leading to the aggregation of C. This indicates that some hydrocarbons were formed and desorbed from SiC by D_2^+ implantation, which is consistent with previous reports that only methane is desorbed from SiC, although silane is not formed [12, 13]. Carbon vacancies were introduced and Si with dangling bonds remained in SiC, which would be the major D trapping sites in SiC. This behavior can also be assumed for the gamma-ray irradiation case. The ratio of C aggregation on the surface would be quite small because the electron excitation process induced the dissociation of a single Si-C bond while another Si-C bond still remained. However, these Si and C atoms with the dangling bond could be potential hydrogen isotope trapping sites. This can be explained by the fact that the extent of desorption of D as the C-D bond as seen in the TDS spectra was higher than that for Fe^{3+} irradiated SiC. In addition, the in-situ D_2 gas exposure during gamma-ray irradiation clearly showed that some of the dangling bonds quickly recombined and the D present quickly interacted with these dangling bonds, leading to the enhancement of D retention. It can be concluded that the collision process induces the dissociation of SiC matrix and C aggregates near the surface region, but the electron excitation process can dissociate a single Si-C bond and D trapping by dangling bonds can enhance D retention in SiC.

4. Conclusions

Two different radiation techniques, Fe^{3+} irradiation and gamma-ray irradiation, were utilized to evaluate the radiation effect on hydrogen isotope retention in SiC. It was found that the D_2 TDS spectra included two desorption stages, namely the desorption of D bound to Si as a Si-D bond and C as a C-D bond. It was found that the damage introduced by Fe^{3+} irradiation produced displaced carbon atoms in SiC, which led to the dynamic D desorption. For gamma-ray irradiation, C or Si with the dangling bond was formed uniformly throughout the SiC matrix. It was presumed that the electron excitation process by gamma-ray irradiation dissociated a single Si-C bond and D trapping by dangling bonds enhanced D retention. However, the collision process by Fe^{3+} irradiation could induce the dissociation and aggregation of C near the surface region, leading to less D retention.

Acknowledgments

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