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Effect of Energetic Helium ion Implantation on Hydrogen Isotope Retention in Silicon Carbide

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The effects of He retention and damage introduction on the D retention in SiC were studied by changing the implantation energy of He^+ from 0.75 keV to 4.0 keV. The D and He retentions in SiC and chemical behavior of SiC were evaluated by means of thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS). It was found that the D retention decreased by the He retention in the same implantation depth with D_2^+, although that increased if the implantation depth of He^+ is larger than that of D_2^+. In addition, free C formation would make the higher retention of D bound to C. These facts indicate that not only the introduction of damaged structures but also the He retention would govern the hydrogen isotope retention in SiC.

Keywords: Tritium retention Helium ion implantation effect, silicon carbide, XPS, TDS

1. Introduction

Silicon carbide (SiC) is thought to be one of candidates for an insulating insert in the Pb-Li channels of the dual-coolant breeding blanket concept, due to its minimal activation, good compatibility with Pb-Li, good thermal conductivity and thermal stability [1-4]. One of the critical issues is the evaluation of hydrogen isotope retention and its helium implantation effects for evaluating the tritium transport in the blanket system. In our previous studies, it was found that the deuterium was preferentially trapped by C and, thereafter, it was trapped by Si, which was the major deuterium trapping state in SiC [5]. However, in the case of helium implantation, it was trapped by both of Si and C even in the low hydrogen isotope ion fluence, indicating the helium implantation would make a large influence on hydrogen isotope trapping [6-9]. In addition, helium pre-implantation and post-implantation experiments show that the retention of deuterium bound to C was almost constant even in the helium pre-implantation and post-implantation experiments, although that bound to Si largely decreased especially in the helium post-implantation. These facts indicate that helium would correlate with the deuterium bound to Si and this would be the results of the conjunction of helium retention and damage introduction. This motivates us to understand more detail interaction mechanism of helium and damaged structures on hydrogen isotopes in SiC.

In this study, the helium ion (He^+) implantation energy was systematically changed from 0.75 keV to 4.0 keV, which corresponded to the implantation depth of 5 - 40 nm, and, thereafter, 1.0 keV of deuterium ion (D_2^+) (implantation depth of 10 nm) was implanted. The effect of He implantation on deuterium retention was studied by X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS).

2. Experimental

A polycrystalline silicon carbide (β-SiC) wafer (ROICERAM-HS) supplied by Asahi Glass Co. Ltd., with a size of 10 mm^{ϕ}×0.5 mm^{t} was used as a sample. The sample was heated at 1300 K for 10 minutes in a vacuum below 1×10^{-6} Pa to remove residual hydrogen and impurities as a pretreatment. After cooling, He^+ was implanted with an energy of 0.75 - 4.0 keV using an ion flux of 1.3×10^{18} He^+ m^{-2} s^{-1} and an ion fluence of 1.0×10^{22} He^+ m^{-2} at room temperature. Thereafter, 1.0 keV D_2^+ implantation was performed using the same ion flux and fluence. The implantation depth of 0.75 - 4.0 keV He^+ by SRIM calculation was evaluated to be about 5 - 40 nm, although that of 1.0 keV D_2^+, 10 nm [10]. This fact shows that He^+ with an energy of 0.75 keV retains in the near surface region and deuterium, beneath the He^+ retention region, although in case of He^+ with an energy of 4.0 keV, the retention region of He^+ and D_2^+ was replaced and the deuterium is retained in the surface region. After these experimental sequences, the chemical states of Si and C were evaluated by XPS (ESCA1600 system, ULVAC-PHI Inc.) [5-9]. To evaluate the D and He retentions, TDS experiments using a high resolution mass spectrometer were performed at a heating rate of 0.5 K s^{-1} and at heating temperature up to 1300 K.

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3. Results and discussion

Fig. 1 shows D_2 and He TDS spectra obtained for SiC with various He^+ implantation energies. It was found that D_2 TDS spectra for the 0.75 keV and 1.3 keV He^+ implanted SiC consisted of two desorption peaks, and trapping state is almost the same as that of non- He^+ implantation experiment as shown in our previous paper, where the desorption temperature was slightly shifted to lower temperature side. However the desorption stages are almost consistent with the previous paper [5]. For the 4.0 keV He^+ implanted SiC, an additional desorption peak was observed at the temperature around 1200 K, which has not observed for the He^+ implantation with the same implantation depth with D_2^+. In addition, the FWHM (full width at half maximum) was quite narrow, indicating that the desorption process was quite different from the other desorption stages of Si-D and C-D bonds. It was confirmed that this desorption peak was clearly associated by the desorption of D_2, not He and the reproducibility was confirmed. The He TDS spectra in Fig. 1(b) indicated that large amount of He was desorbed for the 4.0 keV He^+ implanted SiC at the desorption temperature of about 1200 K, indicating that the D desorption would be accompanied with the He desorption. However, no large desorption peak was observed for the 0.75 keV and 1.3 keV He^+ implanted SiC samples, which lead to the direct interaction between He and D. From the TDS spectra, the D and He retentions were summarized in Fig. 2, indicating that the large D retention was found for the 4.0 keV He^+ implanted SiC,

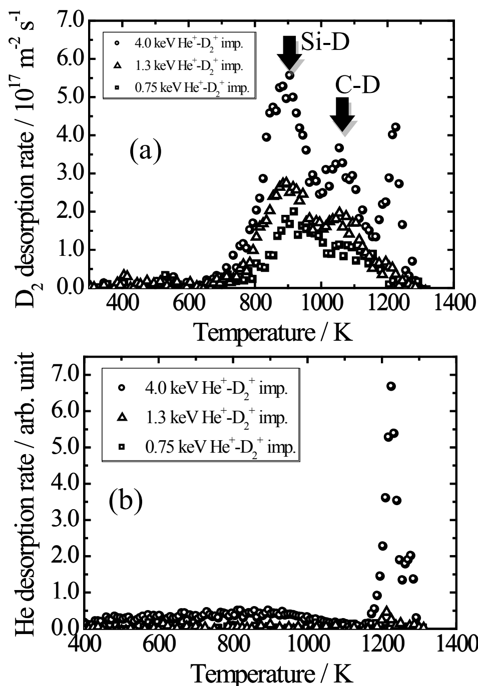

Fig. 1 The (a) D_2 and (b) He TDS spectra for the He^+ implanted SiC with the implantation energy of 0.75 keV, 1.3 keV and 4.0 keV. The implantation energy of D_2^+ was set to be 1.0 keV.

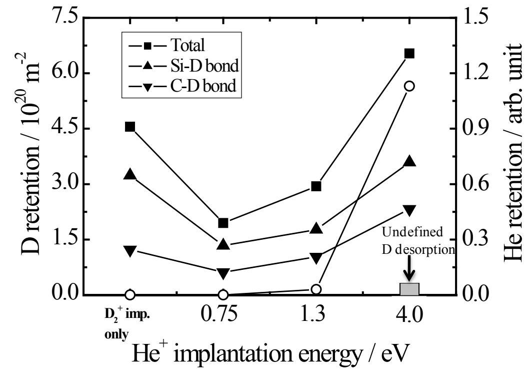

Fig. 2 Summary of D and He retentions for the He^+ implanted SiC with the implantation energy of 0.75 keV, 1.3 keV and 4.0 keV.

although those for the 0.75 keV and 1.3 keV He^+ implanted SiC samples were almost constant, indicating that the He retained near surface region would interfere D trapping.

Fig. 3 shows the XPS spectra of Si 2p and C 1s as a function of He^+ implantation energy and peak positions of Si 2p and C 1s were summarized in Fig. 4. It was found that the peak positions of C 1s for 1.3 keV and 4.0 keV He^+ implanted SiC samples were shifted toward higher energy side, although that for 0.75 keV was moved to lower energy side, indicating that the damaged structures were introduced in the near surface region by high energy He^+ implantation. In the case of 0.75 keV He^+ implantation, not only the damage introduction but also He retention would make the negative peak shift. However, after the D_2^+ implantation, the peak positions for all the samples were shifted toward higher energy side, showing the D retention in SiC. For Si 2p, which is largely influenced by the defect around the Si atom, the negative peak shift was observed, indicating the introduction of C defects. By the D_2^+ implantation, the peak positions were slightly shifted toward the original position. This would be the indication of Si-D formation. The peak areas of C 1s and Si 2p were summarized in Fig. 5. It was found that the peak areas of C 1s decreased by He^+ and D_2^+ implantation, although those of Si 2p were almost constant. This indicates that the selective chemical sputtering of C was occurred for SiC and free C would be formed.

Based on these experimental results, the interaction between hydrogen isotopes and helium, and damaged structures in SiC are discussed. As mentioned in our previous paper [5], it is considered that most of hydrogen isotopes implanted with high energy are bound to Si and C with forming Si-D and/or C-D bonds. According to the SRIM calculation, the 4.0 keV He^+ was retained beneath the D retained region because the implantation depth of He was much higher than that of D, indicating that only the damaged structures would make a large influence on the D retention, although both of the introduction of damage

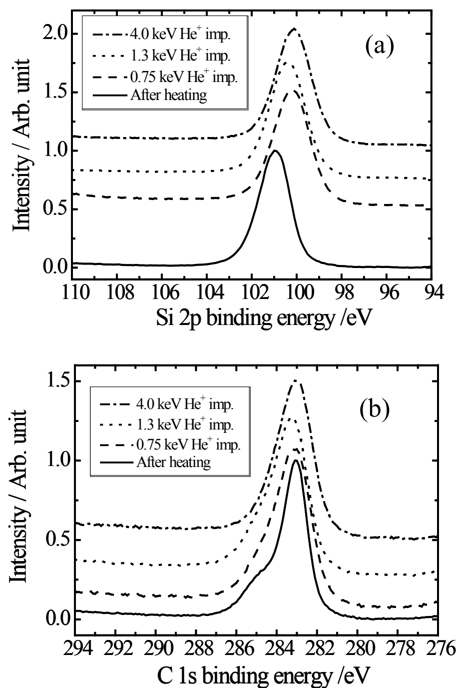

Fig. 3 XPS spectra of (a) Si 2p and (b) C 1s for the He^+ implanted SiC with the implantation energy of 0.75 keV, 1.3 keV and 4.0 keV.

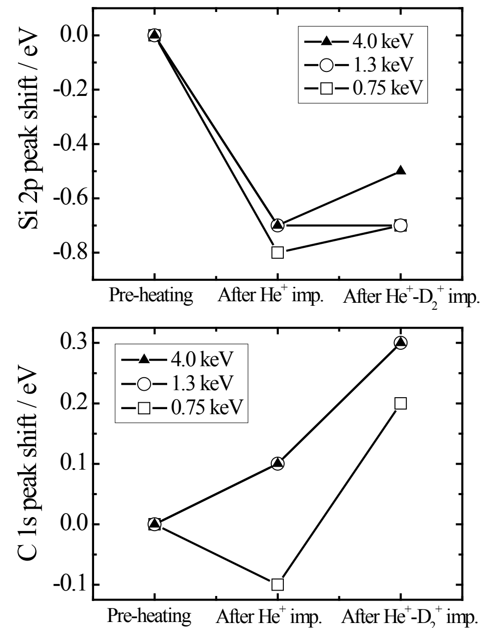

Fig. 4 Summary of peak shifts of (a) Si 2p and (b) C 1s for the He^+ implanted SiC.

structures and He retention govern the D retention in case of 0.75 keV and 1.3 keV He^+ implantation as mention above. Therefore, it can be said that the D retention in SiC increased by the introduction of the damaged structures, although the amorphization did not confirm in the present study. It is reported that the Si-Si bonds were formed after electron irradiation, while the no C-C bonds formation was observed in the reference papers by S. Muto et al., which was explained by simple molecular orbital calculations [11-12]. This result is also consistent with our experimental results, showing that the retention of D bound to Si was almost the same as that for the non-He^+ implanted SiC, although the retention of D bound to C was increased by high energy He^+ implantation. In addition, some papers mentioned that the recrystallization would be preceded at the temperature above 2000 K. Therefore the damaged structure would remain in the sample even if the deuterium is desorbed [13,14]. According to Si 2p XPS spectra, there was no large difference between just after He^+ implantation and additional D_2^+ implantation, indicating that Si-Si cluster was formed by He^+ implantation. It can be said that the free C would be formed by He+ implantation and made the C-D formation at room temperature. In addition, the undefined desorption stage was found at the temperature of 1200 K, which is the same temperature of He desorption from He bubble, indicating that the He bubble decomposition triggered the this D desorption. However, the detailed mechanism is still not clear and further studies will be required to elucidate this desorption process.

By the He^+ implantation with higher energy, large amount of damaged structure was introduced and the D was trapped in SiC, making negative peak shift of Si 2p and positive peak shift of C 1s. In addition, in case of C 1s, free C formation would induce the positive peak shift of C 1s by the He^+ implantation. More peak shift toward higher binding energy side was found by the D_2^+ implantation, showing the formation of C-D bond and induction of the chemical sputtering of C. It is also reported that the carbon interstitials can freely migrate while the Si interstitials are immobile around room temperature [12]. This fact was also consistent with our experimental results that the free C was aggregated on the surface by heating after the He^+ and/or D_2^+ implantations. In case of low He+ implantation, large amount of He was retained in the same project range of D. This He retention prevents the D trapping by Si as shown in our previous paper [6-9]. In addition, the He retention in SiC would prevent the D retention. This would be explained by the Si-Si clusterization and/or He retention in the diffusion path of D in SiC, which induce the high D de-trapping efficiency.

In summary, the 4 keV He^+ implantation, which penetration depth is higher than that of 1 keV D_2^+, introduces the damaged structure in SiC, which explains the higher D retention compared to that of 0.75 keV He^+ implantation . This fact indicates that the He retention would be one of the key factors for the evaluation of hydrogen isotopes retention in SiC.

4. Conclusion

The effect of He retention and damage introduction on the D retention in SiC were studied as a function of the

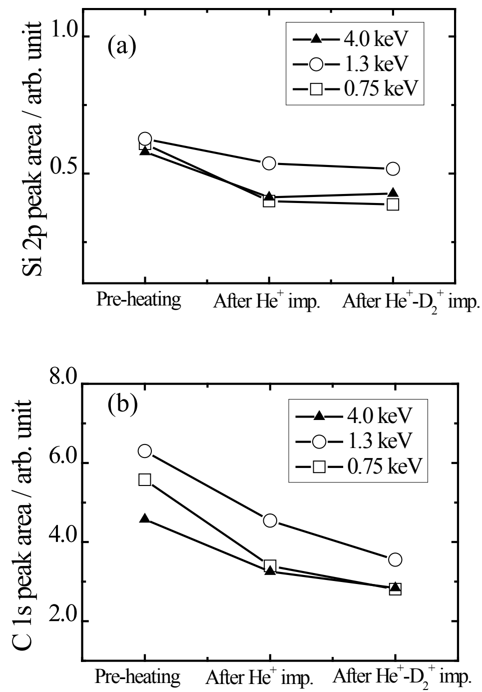

Fig. 5 Summary of peak areas of (a) Si 2p and (b) C 1s for the He^+ implanted SiC.

implantation energy of He^+ from 0.75 keV to 4.0 keV. The D and He retentions in SiC and chemical behavior of SiC were evaluated by means of XPS and TDS. It was found that the D retention decreased by the He retention in the same implantation depth with D_2^+, although that increased if only the damaged structures were introduced. It can be said that the energetic D_2^+ was directly interacted with the retained He near the surface region and both of He and D would be quickly desorbed, which induced the low He and D retentions in SiC. However, in the case of He retention beneath the D retention region, large He retention was observed. In addition, free C formation would make the high retention of D bound to C. These facts indicate that not only the damage introduction but also the He retention governs the hydrogen isotope retention in SiC.

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