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Effects of helium irradiation on chemical behavior of energetic deuterium in SiC

T. Sugiyama [a,*], Y. Morimoto [a], K. Iguchi [a], K. Okuno [a], M. Miyamoto [b], H. Iwakiri [b], N. Yoshida [b]

[a] Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, 836 Oya, Shizuoka-shi, Shizuoka-ken 422-8529, Japan

[b] Research Institute for Applied Mechanics, Kyusyu University, 6-1 Kasugakouen, Kasuga-shi, Fukuoka 816-8580, Japan

Abstract

Structural changes of SiC caused by deuterium (D_2^+) and helium ion irradiation were studied with X-ray photoelectron spectroscopy (XPS) for ion energies in the range from 0.5 to 3.0 keV. Thermal desorption spectroscopy (TDS) measurements were performed to study the desorption processes from SiC surfaces pre-irradiated with deuterium and helium of 10 and 8.0 keV ion energy, respectively. For both ion species the range is approximately the same. The XPS experiments showed that the carbon concentration in the vicinity of the SiC surface was reduced owing to the helium irradiation. This suggests that carbon was selectively sputtered by the helium irradiation. In the TDS experiments, the D_2 desorption was found to consist of three processes. The activation energy and the released amounts of deuterium for each peak were affected by helium pre-irradiation.

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1. Introduction

Silicon carbide, SiC, has been proposed as a candidate for plasma facing materials due to its low activation. The Evaluation of the chemical behavior of hydrogen isotopes in plasma facing materials (PFM) is necessary to understand the recycling process for hydrogen isotopes in fusion reactors. For the tritium inventory in PFM this behavior is of high concern for D–T fusion reactors. Therefore, we have carried out studies on the retention of energetic D in SiC [1,2]

In the D–T plasma, plasma facing materials are exposed to energetic helium produced by the fusion reaction, and also to energetic helium during the helium discharge cleaning. Therefore, we must consider helium irradiation effects on the chemical behavior of hydrogen isotopes in plasma facing materials. Only helium retention properties and helium irradiation effects on mechanical properties of SiC have been studied [3,4]. However, helium irradiation effects on the chemical behavior of energetic hydrogen isotopes in irradiated SiC have not been studied yet.

In the present study, the effects of helium irradiation on the chemical behavior of deuterium in irradiated SiC were investigated by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). Structural changes of SiC caused by deuterium and helium ion irradiation were studied with XPS. The desorption processes of the irradiated deuterium and helium were analyzed with TDS using a high-resolution quadrupole mass spectrometer (HR-QMS).

2. Experimental

2.1. X-ray photoelectron spectroscopy

The specimens consist of β-silicon carbide (SiC) and were prepared by Asahi Glass Corporation (ROICERAM-HS). The size was ∅ 10 mm × 1 mm.

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[*] Corresponding author. Tel.: +81-54 238 6436; fax: +81-54 238 3989.

E-mail address: r0032007@ipc.shizuoka.ac.jp (T. Sugiyama).

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The XPS system is composed of an electron spectrometer, a MgKα X-ray source and an ion source, and is installed in the spectrometer chamber. The electron spectrometer is a hemispherical electrostatic-type energy-analyzer.

The experimental procedure: after cleaning the specimen by argon sputtering, which was carried out at an incident angle of 60 degrees for the sample, the surface was analyzed by measuring the narrow-energy-range C1s and Si2p spectrum with XPS. Sensitivity factors were used. The sensitivity of C1s and Si2s are 1.000, and 1.145, respectively [5]. Then, the sample was irradiated with deuterium (D_2^+) or helium ions (He^+). The impact energies of deuterium and helium were varied in the range from 0.5 to 3.0 keV (0.25–1.5 keV per D-atom). Those ion irradiations were performed at an angle of 90° to the sample after the ion irradiation.

The sample was analyzed again after the ion irradiation. The deuterium or helium ion irradiation and the XPS measurement were repeated sequentially until the ion fluence reached 1.0×10^{22} m^{-2}. After that, argon sputtering and XPS measurements were sequentially carried out to measure the depth profiles of SiC. The argon sputtering was performed with 1.0 keV Ar^+ of 2.79×10^{17} $m^{-2}\,s^{-1}$ for 3600 s.

2.2. Thermal desorption spectroscopy

The sample used in the TDS experiments was same as that in the XPS experiments. In order to elucidate the effects of helium irradiation on the chemical behavior of energetic deuterium in SiC, it was first irradiated with helium ions, and then irradiated with deuterium ions. Ion energies of helium and deuterium, of which both ion ranges were approximately the same, were 8.0 and 10 keV, respectively. The ion fluences of helium and deuterium were varied up to 1.0×10^{22} m^{-2}. The irradiation temperature of the sample was room temperature (RT). After helium and deuterium irradiation, the sample was heated from RT to 1600 K with different heating rates between 0.5 and 1.75 $K\,s^{-1}$. During heating, the desorption rates of helium (^4He) and deuterium (D_2) were measured with a HR-QMS (HIRESON-2SM), which is able to discriminate deuterium (D_2: 4.0282 amu) from helium (He: 4.0026 amu) [6].

The obtained TDS spectra were analyzed by the Gaussian distribution function, and each peak temperature was determined from the analyzed spectra. Each peak area was calculated by integrating the desorption rate. In addition, the activation energy of each desorption process for deuterium was estimated by Arrhenius plots of the peak temperature determined with the different heating rates [7,8].

3. Results

3.1. X-ray photoelectron spectroscopy

Fig. 1 shows the dependence of the C1s and Si2p peak areas on the deuterium ion fluence. The C1s peak area decreases with increasing deuterium ion fluence. The Si2p peak area decreases up to 10^{21} D m^{-2}. However, it increases with increasing the deuterium ion fluence above 10^{21} D m^{-2}. A similar phenomenon was observed in the case of the helium ion irradiation. Those suggest that carbon was selectively sputtered by deuterium and helium ions, compared with silicon.

Fig. 2 shows the depth profile of the C1s binding energy and peak area after the helium irradiation. After the irradiation up to 1.0×10^{22} He^+ m^{-2}, the C1s peak was located at 283.43 eV. When the sample was sputtered with argon ions, the C1s binding energy decreases by 0.2 eV. It can be seen that the C1s peak area decreases with increasing the argon ion fluence up to 2.79×10^{17} Ar^+ m^{-2}, and its further increase results in an increase of the C1s peak area. Because the helium collision with carbon resulted in the reduction of the carbon concentration, the depth of SiC where the C1s peak area became a minimum was considered to be the mean range of helium ions. When a shallower depth than the mean range of helium ion was measured, the C1s binding energy shifted to the high-energy side compared with that of the bulk SiC. This positive shift was attributed to the increase in C–C bonds, because the C1s binding energy of the C–C bonds could be larger than that of the C–Si bonds. It was supposed that the SiC surface became rich with C–C bonds owing to the helium irradiation.

3.2. Thermal desorption spectroscopy

The D_2 TDS spectrum obtained for SiC irradiated with deuterium ion is shown in Fig. 3. The D_2 TDS

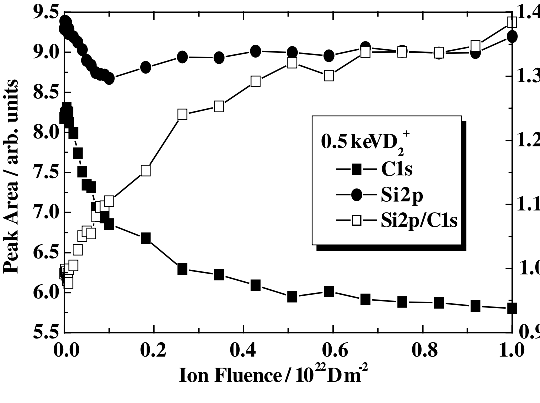

Fig. 1. Dependence of the deuterium ion fluence of 0.5 keV D_2^+ on the the peak area of the C1s and Si2p.

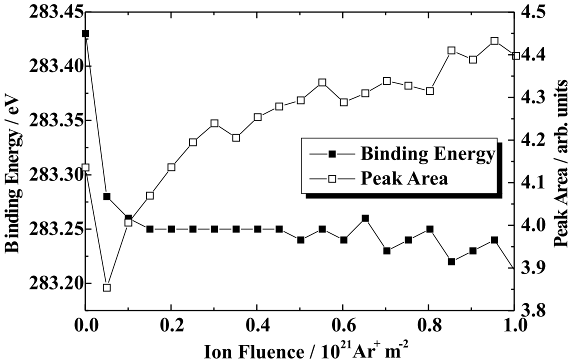

Fig. 2. Depth profile of the C1s binding energy and peak area for SiC irradiated with 2.5 keV He^+ at a fluence of 1.0×10^{22} He^+ m^{-2}.

spectrum was analyzed to consist of three peaks, denoted by peak 1, 2 and 3 in the Figure. This suggests that there are three processes in the D_2 desorption behavior. Each peak area was changed by the helium pre-irradiation. These results are shown in Fig. 4. The peak 2 area increased with increasing the helium pre-irradiation, while the peak 3 area decreased. The sum of the peak 2 and the peak 3 area was constant, being independent of the ion fluence of the helium pre-irradiation. This suggests that the deuterium, which should be trapped in the trapping site for peak 3, transferred to that for peak 2 by the helium pre-irradiation. The amount of transferred sites depends on the helium ion fluence. Therefore, the reduction of the peak 3 area could be correlated with the selective carbon reduction around the mean range of helium ion, as shown in Fig. 2. But the peak 1 area was scarcely affected by the helium pre-irradiation.

In order to reveal the chemical behavior of deuterium irradiated into SiC, the activation energy of the deuterium desorption was obtained by varying the heating rate. The activation energies for peak 1, 2 and 3 were determined to be 2.31 ± 0.50, 3.12 ± 0.17, and (3.70 ± 0.76) eV, respectively, as shown in Table 1.

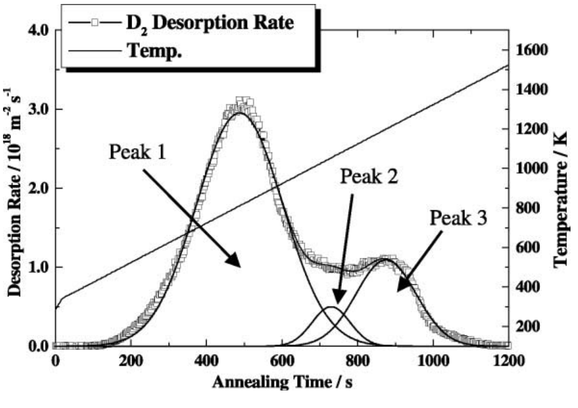

Fig. 3. TDS spectrum after 10 keV D_2^+ irradiation at a fluence of 1.0×10^{22} He^+ m^{-2}.

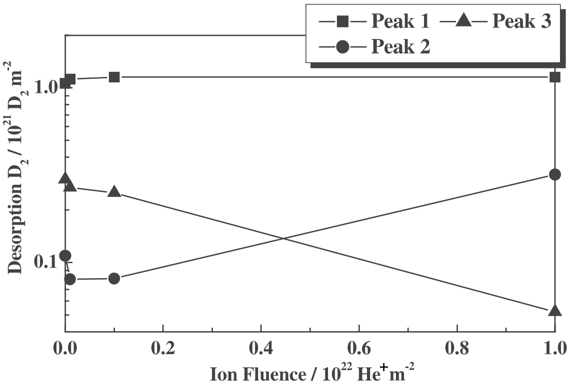

Fig. 4. D_2 desorption in dependence on the ion fluence of the helium pre-irradiation.

Table 1
The activation energy of the deuterium desorption from SiC

Peak no.	Activation energy (eV)		
	Without He pre-irradiation	10^{21} He^+ m^{-2}	10^{22} He^+ m^{-2}
Peak 1	2.31 ± 0.50	1.59 ± 0.11	2.48 ± 0.45
Peak 2	3.12 ± 0.17	3.47 ± 1.24	4.45 ± 0.58
Peak 3	3.70 ± 0.76	4.37 ± 0.95	5.04 ± 1.22

Not only the peak area but also the activation energy for peak 2 and 3 was changed by the helium pre-irradiation, as shown in Fig. 4 and Table 1, respectively. On the other hand, there were no changes for peak 1. The increases in the activation energy of the deuterium desorption for peak 2 and 3 could be attributed to the structural changes of SiC caused by the helium pre-irradiation.

4. Discussion

We will first consider the trapping sites of deuterium irradiated into SiC from the view point of the activation energy of deuterium desorption. The activation energy was determined to be (2.31 ± 0.50) eV (peak 1), (3.12 ± 0.17) eV (peak 2), and (3.70 ± 0.76) eV (peak 3), as listed in Table 1. The activation energy for the desorption of hydrogen dissolving in silicon was reported to be 0.50 eV [9]. In other words, the activation energy of diffusion energy is 0.50 eV. This suggests that existing states of deuterium irradiated in SiC should not be in the interstitial sites. The binding energy of the Si–H and C–H bond was reported to be (2.80–3.90) eV and

(3.50–4.80) eV, respectively [11–13]. Without pre-helium irradiation, almost all irradiated deuterium was trapped by peak 1 and 3 states. It, therefore, is believed that the peak 1 and 3 are due to the detrapping from the Si–D and C–D bond, respectively.

Secondly, we discuss the dependence of the pre-helium irradiation in SiC on the deuterium ion fluence in order to reveal the deuterium desorption behavior for the peak 2. Increases in the helium ion fluence of the pre-helium irradiation led to the following experimental results described below. In the mean range of helium ions, the carbon concentration decreased much. In the vicinity of the SiC surface, the carbon concentration decreased compared to the bulk. In addition, the recoil carbon recombined with carbon during helium pre-irradiation. Therefore, the amount of C–C bond was increased with decreasing C–Si bonds, and the desorption behavior of the trapped deuterium was changed. Without the pre-helium irradiation, almost all of irradiated deuterium was trapped by silicon and carbon that did not almost received structural changes (elucidated by XPS measurement that almost all Si in SiC associated with C in SiC to make the Si–C bond.). When the pre-helium irradiation was performed, an appreciable increase in the peak 2 area was observed as shown in Fig. 4. It was thought that the increase in the peak 2 area was due to the increase of C–C bonds on the SiC surface. In addition, the activation energy determined for the peak 2, (3.12 ± 0.17) eV, was comparable to the binding energy of the C–H bond on the carbon surface, 2.94 eV, reported previously [10]. It is believed that the peak 2 is due to the detrapping from the C–D bond in the carbon rich surface.

The dependence of the three desorption processes for deuterium from the SiC pre-irradiated by helium was evaluated from the change of activation energies, as follows. The activation energy of the peak 2 and 3 changed as well as the peak area of both peaks (in Fig. 4), while that of the peak 1 was not observed to change, as shown in Table 1. Because of structural changes of SiC caused by helium pre-irradiation, the activation energy of the desorption for peak 2 and 3 increased. The helium pre-irradiation influenced the desorption from the C–D bond (peak 2 and 3), and did not influence the desorption from the Si-D bond (peak 1). It, therefore, seems reasonable to conclude that the helium pre-irradiation disordered the carbon structure of SiC and it was hard for the deuterium to repeat the detrapping and trapping from its disordered carbon. It can be assumed that irradiated helium existing in the vicinity of the disordered carbon disturbed deuterium to repeat the detrapping and trapping and then lead to an increase in the activation energy of the deuterium desorption. In order to discuss this in detail, further experiments on existing states of helium in SiC could be required.

5. Summary

In this paper, the effects of helium irradiation on the chemical behavior of deuterium irradiated in SiC was investigated by means of XPS and TDS. The XPS experiments showed that the carbon concentration in the vicinity of the SiC surface was reduced by helium irradiation, and the SiC surface was enriched with C–C bonds. The TDS experiments showed that there were three D_2 desorption processes, the activation energies of the deuterium desorption for each peak were determined. Comparing our determined activation energies with the literature values, the desorption of deuterium from trapping sites of each peak could be attributed to C–Si-D, C–C–D and Si–C–D. The present study made clear that the helium pre-irradiation influenced the desorption behavior of the deuterium trapped in the SiC.

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