

Helium irradiation effects on retention behavior of deuterium implanted into boron coating film by PCVD

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Abstract

Helium irradiation effects on the retention of energetic deuterium implanted into the boron coating film were investigated by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). It was found, by XPS, that the B 1s peak was shifted to lower binding energy side by He⁺ ion irradiation and the FWHM was extended. These facts show that the some defects were introduced into the boron coating film by He⁺ ion irradiation. From TDS experiment, the deuterium retention, especially the amount of B–D terminal bond, increased by the pre-He⁺ ion irradiation. However, it decreased by the post-He⁺ ion irradiation. These experimental results indicate that the B–D terminal bond was mainly influenced by the He⁺ ion irradiation because the two neighbor B–D bonds have to dissociate simultaneously for the B–D–B bridge bond.

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1. Introduction

Boronization as wall conditioning has been performed on a lot of fusion test devices and remarkable improvement on the plasma performance has been achieved [1–6]. In the future fusion devices, helium will be produced by the thermonuclear reactions and be thought to interact with the boron coating film. There-

fore, it is considered that energetic helium will influence the hydrogen isotope retention.

In our previous studies, the boron coating film with carbon impurity was studied and it was found that the contribution of hydrogen isotope retention was enhanced by the contained carbon [7,8]. For the pure boron coating films, although the hydrogen isotope retention decreases, the hydrogen isotope was trapped by boron with forming B–D–B bridge bond and B–D terminal bond, and their activation energies were estimated to be 1.11 ± 0.21 eV and 2.17 ± 0.36 eV, respectively [9,10]. To simulate hydrogen isotope behavior on the first wall in fusion reactors, it is important to study

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the helium irradiation effects on the retention and chemical behavior of hydrogen isotopes. Therefore, in this study, helium irradiation effects for the retention of energetic deuterium implanted into the boron coating film were investigated by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). The hydrogen isotope behavior in the boron coating film has systematically discussed.

2. Experimental

2.1. Preparation of boron coating film by PCVD

Pure boron coating films were deposited on silicon substrates by using a decaborane gas diluted with helium gas by plasma chemical vapor deposition with RF-assisted DC glow discharge in the plasma CVD (PCVD) apparatus [9]. The PCVD process chamber was evacuated to less than 10^{-6} Pa, and decaborane and helium gases were introduced into the chamber with the flow rates of 2.5 sccm and 3.8 sccm, respectively. The pressure of the chamber was kept at 25.0 Pa and the temperature of the substrate at 673 K during the PCVD process. The thickness of the film was evaluated by XPS depth profiling with Ar^+ sputtering (ESCA1600, ULVAC-PHI Inc. Al-K α 400 W) and was found to be about 120 nm. Table 1 shows the atomic composition ratio of the prepared boron coating film. It was found that the atomic composition ratio of boron in the film was reached to be 0.96.

2.2. Hydrogen isotope behavior in pre- and post- He^+ ion irradiated boron coating film

The achieved boron coating film was heated at 1200 K for 30 min before the helium (He^+) and deuterium (D_2^+) ions irradiation experiment to remove the residual hydrogen. Two kinds of experiments, namely pre- and post- He^+ ion irradiation experiments were performed. In the pre- He^+ ion irradiation experiment, the 0.8 keV He^+ ions were irradiated to the sample with the flux of $1.2 \times 10^{18} \text{ He m}^{-2} \text{ s}^{-1}$ up to the fluence of $1.0 \times 10^{22} \text{ He m}^{-2}$. Thereafter, the 1.0 keV D_2^+ ions were irradiated to the sample with the flux of $1.5 \times 10^{18} \text{ D m}^{-2} \text{ s}^{-1}$.

Table 1

Atomic composition ratio of the prepared boron coating film estimated by XPS

	Atomic composition ratio
Boron	0.96
Carbon	0.03
Nitrogen	0.00
Oxygen	0.01

s^{-1} up to the fluence of $1.0 \times 10^{22} \text{ D m}^{-2}$. The project ranges of D and He were, respectively, found to be 20 nm and 26 nm by TRIM code and set to be almost the same. The chemical state of boron was studied by XPS after each irradiation experiment. The desorption behavior of deuterium and helium from the boron coating film was also evaluated by TDS with the heating rate of 0.5 K s^{-1} up to 1200 K using a high resolution mass spectrometer (Microvision Plus 1-6 D, MKS, Inc.). For the post- He^+ ion irradiation experiment, the D_2^+ ions were irradiated into the boron coating film with the accelerated energy of 1.0 keV at the same flux and fluence as the pre- He^+ irradiation experiment. After D_2^+ ion irradiation, 0.8 keV He^+ ions were also irradiated with the same experimental conditions with the pre- He^+ ion irradiation experiment.

3. Results

Fig. 1 shows the XPS spectra of B 1s in pre- He^+ ion irradiation experiment. It was found that the initial B 1s peak position was located at 188.0 eV and its FWHM was 2.1 eV. After He^+ ion irradiation, the peak position was shifted to lower binding energy side, 187.3 eV and its FWHM was extended to 2.7 eV. These facts indicate that the some defects were introduced into the boron coating film and boron with dangling bonds would exist. This peak was shifted to higher binding energy side after D_2^+ ion irradiation. The FWHM of 2.8 eV after D_2^+ ion irradiation was clearly wider than that after He^+ ion irradiation. This peak shape was different and the FWHM was more extended compared to that D_2^+ ion irradiation without He^+ ion irradiation as shown in our previous study [10]. It can be said that the some dangling bond would bind to deuterium and some of the defects would remain in the boron coating film. Therefore,

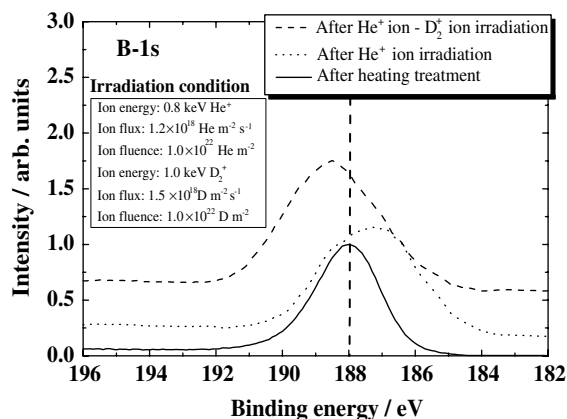


Fig. 1. XPS spectra of B 1s for the boron coating film in the pre- He^+ ion irradiation experiment.

the hydrogen retention may increase by He^+ ion irradiation.

For the post- He^+ irradiation experiment, the B 1s peak position was shifted to higher binding energy side after D_2^+ ion irradiation as shown in Fig. 2. This peak was extended to lower binding energy side by the post- He^+ irradiation. This result indicates that the some defects were considered to be introduced in the boron coating film.

Fig. 3 shows the summary of the XPS spectra for pre- and post- He^+ ion irradiation experiments and after heating treatment without He^+ ion irradiation. It was found that the XPS spectrum for the pre- He^+ ion irradiation experiment was shifted to higher binding energy side and its FWHM is the largest in the experimental results. Therefore, lots of deuterium would be introduced in the

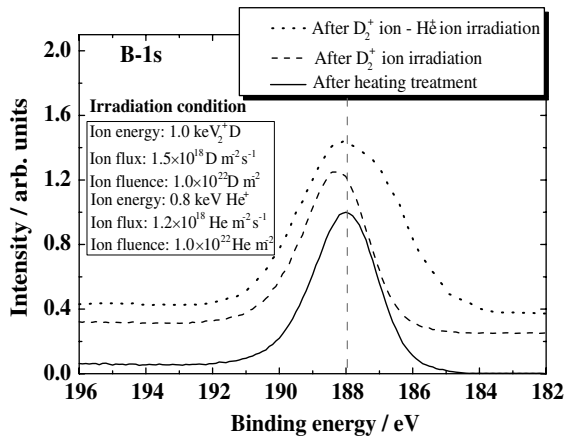


Fig. 2. XPS spectra of B 1s for the boron coating film in the post- He^+ ion irradiation experiment.

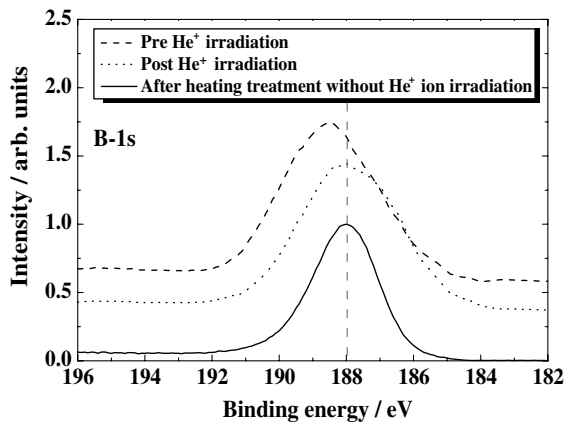


Fig. 3. XPS spectra after He^+ and D_2^+ ion irradiation for pre- and post- He^+ ion irradiation, and after heating treatment.

pre- He^+ ion irradiation. However, the B 1s spectrum for the post- He^+ ion irradiation experiment was shifted to the lower binding energy side and the contribution of defects to B 1s peak shift is larger than that for pre- He^+ ion irradiation. Therefore, the retained deuterium would be desorbed by the post- He^+ ion irradiation.

To estimate the deuterium retention and elucidate its desorption behavior from the boron coating film, TDS experiments were performed. Fig. 4 shows the TDS spectra of D_2 ($m/e = 4$) for pre- and post- He^+ ion irradiation experiments and just after D_2^+ ion irradiation without He^+ ion irradiation. It was found that the deuterium desorption stage after D_2^+ ion irradiation consisted of two stages, namely 1st stage at around 450 K and 2nd stage at around 600 K. In the previous reports, these two peaks were assigned to be the desorption stages of deuterium bound to boron with forming B–D–B bridge bond and B–D terminal bond, respectively [10–13]. The peak intensity from the 2nd stage increased by pre- He^+ ion irradiation. It can be said that the density of the trapping site increased by He^+ ion irradiation and the deuterium could be easily trapped by boron. In contrast to the pre- He^+ ion irradiation experiment, the deuterium retention decreased slightly by the post- He^+ ion irradiation. This result shows that the trapped deuterium was de-trapped by the post- He^+ ion irradiation. The deuterium retention after D_2^+ ion irradiation was normalized to be unity and the retention behavior was summarized in Fig. 5. These trapping and de-trapping behaviors of deuterium with forming B–D bond were enhanced by He^+ ion irradiation compared to that with forming B–D–B bond.

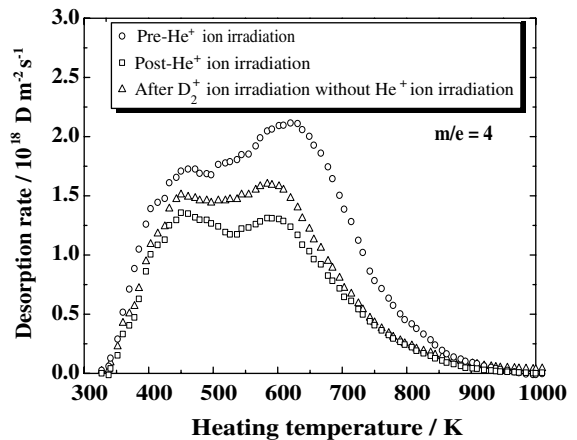


Fig. 4. Thermal desorption spectra of D_2 obtained from boron coating film for pre- and post- He^+ ion irradiation experiment and after deuterium irradiation.

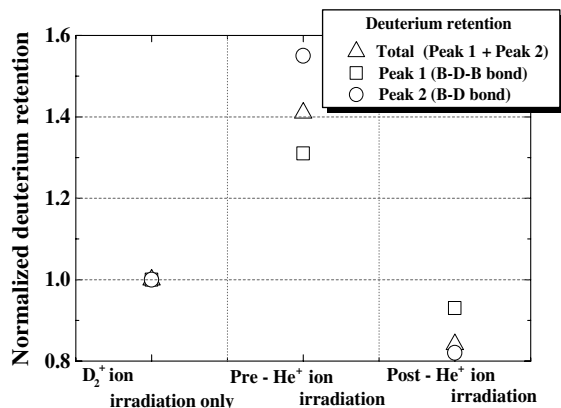


Fig. 5. Deuterium retention in the boron coating film for pre- and post-He⁺ ion irradiation experiment and after deuterium irradiation.

4. Discussion

From these experimental results, the trapping and de-trapping behavior of deuterium in the boron coating film was discussed. The trapping site of B–D–B bridge site would be a unique configuration and chemical state because the trapped deuterium has to interact with neighbor two boron atoms. In typical boron crystal, the B–B length is more than 0.8 nm and it is difficult to configure B–D–B bridge bond in the pure crystal. Therefore, the trapping site for B–D–B bridge configuration is thought to be limited in the boron coating film and would be almost saturated after D₂⁺ ion irradiation. No more the site for B–D–B bond will be produced by the He⁺ ion irradiation because the length of B–B bond is much enough shorten for forming B–D–B bond from the estimation by Gaussian code. Therefore, only the amount of deuterium trapping site for forming B–D terminal bonds increase after He⁺ ion irradiation. In the case of post-He⁺ ion irradiation, the two neighbor B–D bonds have to dissociate simultaneously to desorb the deuterium with forming B–D–B bridge bond. Once one of B–D bonds in B–D–B bridge bond was terminated by He⁺ ion irradiation, it would be easily recombined with dissociated neighbor boron again. Therefore B–D terminal bond was dissociated and only the peak for the 2nd stage in TDS spectra would decrease by the post-He⁺ ion irradiation.

It was concluded that the amount of deuterium with forming B–D bond was mainly influenced by the He⁺ ion irradiation. The deuterium retention for the pre-He⁺ ion irradiation experiment increased up to 1.4 times that without He⁺ ion irradiation. This fact indicates that He⁺ ion irradiation effect should be taken into account for the fusion safety estimation. To clarify more detailed behavior of helium in boron coating film, further study will be required and planned.

5. Conclusion

To elucidate the helium irradiation effects on the retention of deuterium implanted into the boron coating film, He⁺ ion was irradiated into the boron coating film before and after D₂⁺ ion irradiation. The chemical state of boron was evaluated by XPS and the deuterium desorption behavior was studied by means of TDS.

It was found, by XPS, that the B-1s peak was shifted to lower binding energy side by He⁺ ion irradiation and moved to higher binding energy side by D₂⁺ ion irradiation. The FWHM was extended by He⁺ ion irradiation. These facts show that the some defects were introduced into the boron coating film by He⁺ ion irradiation. From TDS experiment, the deuterium desorption stage consists of two stages. The deuterium retention, especially the amount of B–D terminal bond, increased by the pre-He⁺ ion irradiation. This means that the trapping site for B–D terminal bond was only enhanced by He⁺ ion irradiation. For the post-He⁺ ion irradiation experiment, the deuterium retention, especially 2nd stage in TDS spectra, decreased. These facts indicate that only B–D terminal bond was dissociated. For B–D–B bridge bond, it would be easily recombined with dissociated neighbor boron again even if one of B–D bonds in B–D–B bridge bond were terminated. Therefore, the helium irradiation effect contributes to the hydrogen isotope retention in the boron coating film.

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