

Implanted hydrogen isotope retention and chemical behavior in boron thin films for wall conditioning

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Abstract

The behavior of hydrogen isotopes in boron was studied by XPS and TDS. The samples used were boron polycrystals and boron thin films produced by plasma CVD using decaborane ($B_{10}H_{14}$) diluted by He gas. The 1.0 keV deuterium ions were implanted into the samples up to fluence of $5.4 \times 10^{21} \text{ D m}^{-2}$ at various temperatures. It was found that deuterium retention at 573 K was decreased less than 35% compared to that at room temperature. The activation energies for B–D–B and B–D bonds were estimated to be 1.11 ± 0.21 and 2.17 ± 0.36 eV for the boron thin film, and 1.36 ± 0.20 and 2.27 ± 0.45 eV for the boron polycrystal, respectively. The B–H distance and the activation energy for the B–H bond were also calculated by the Gaussian 03 code and these were consistent with the experimental values.

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1. Introduction

Plasma facing wall conditioning has been widely applied in magnetic fusion devices to reduce impurities from plasma facing materials. Boronization is one of the most effective methods to reduce the amount of impurities from the first wall and prevent plasma dilution [1–4]. In the Large Helical Device (LHD) at National Institute for Fusion Science (NIFS), boronization was also applied and a remarkable impurity reduction was achieved [5]. However, it is also necessary to take into account the hydrogen recycling from the boron thin film deposited on the first wall. Therefore, not only the chemical behavior of boron, but also the dynamics of implanted hydrogen isotopes in boron and the estimation of tritium inventory in the boron thin film must be evaluated to understand the boronization effect in detail.

In our previous studies [6,7], the purity of boron in the deposited boron thin film was near 60% and lots of carbon was retained as impurity. The contribution of hydrogen isotope retention in the film was enhanced by the contained carbon [6–9] and the interaction between boron and hydrogen isotopes was not clearly established. In this study, the chemical behavior of deuterium implanted in pure boron thin films deposited on a substrate was analyzed by X-ray photoelectron spectroscopy (XPS) and the dynamics of implanted hydrogen isotopes was followed by thermal desorption spectroscopy (TDS). These results were compared with calculations using the Gaussian 03 code to determine the dynamics of implanted deuterium in the boron samples.

2. Experimental

2.1. The preparation of boron thin film by plasma CVD

The plasma CVD (PCVD) apparatus, whose detail was illustrated in Ref. [8], was designed to deposit pure

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boron thin film on a silicon substrate. In the sample preparation, the boron thin film was deposited on silicon substrates by RF assisted DC glow discharge using decaborane ($B_{10}H_{14}$) diluted by He carrier gas. The PCVD process chamber was evacuated to less than 10^{-6} Pa and, the decaborane and helium gases were introduced to the chamber with flow rates of 2.5 and 3.8 sccm, respectively. The pressure of the chamber was kept at 26.7 Pa, and the temperature of the substrate at 673 K during the CVD process. The glow discharge used power of 50 W for 10 min. The thickness of the thin film was monitored by a quartz oscillator and was found to be about 47 nm. After the deposition process, the sample was transferred by the sample transfer vessel from the PCVD apparatus to XPS or TDS apparatus without atmospheric exposure.

2.2. Behavior of hydrogen isotopes in boron thin films

Two kinds of samples, namely boron polycrystal purchased from Furuuchi Chemical Co. Ltd., and the boron thin film deposited on the silicon substrate described above were placed in the high vacuum chamber with pressure less than 10^{-7} Pa and the 1.0 keV deuterium ions (D_2^+) irradiated the sample. The flux varied from 2.0×10^{18} to 5.4×10^{21} $D m^{-2}$, at an incident angle of 0° to the surface normal, at room temperature. The temperature dependence was evaluated with irradiations at temperature between 304 and 773 K. After deuterium ion irradiation, the chemical state of boron was studied by XPS, (ESCA1600, ULVAC-PHI Inc) using a $AlK\alpha$ 400 W X-ray source and a hemispherical electron analyzer.

The desorption behavior of deuterium from the boron samples was also studied by TDS by varying the heating rate between 0.25 and $1.0 K s^{-1}$ up to 1200 K. The TDS apparatus was newly designed to connect the sample transfer vessel and the sample was transferred from the PCVD apparatus under a He gas atmosphere in the transfer vessel. The analysis chamber was evacuated by a turbo molecular pump (500 l/s) that maintained a vacuum of less than 10^{-6} Pa. The activation energy was evaluated using the Redhead equation [10] and these values were compared with the results calculated by Gaussian 03 code [11] with the model chemistries of HF and B3LYP, and the basic set of 6-31 + g (d, p). The space group used in this calculation was $P4_1$ and the crystal structure was optimized by HF.

3. Results and discussion

3.1. Temperature dependence during the deuterium ion irradiation

Figs. 1 and 2 show the XPS spectra of B 1s for the boron thin film and the boron polycrystal at various

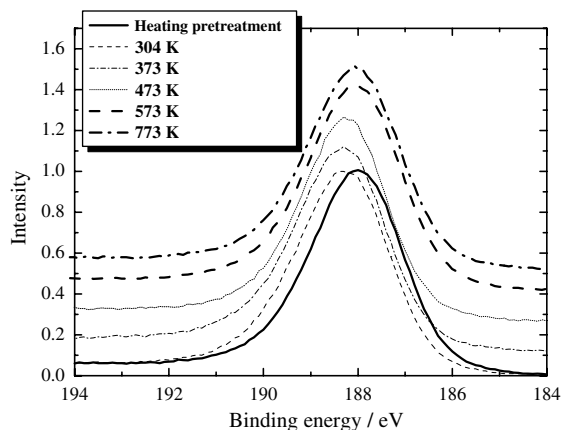


Fig. 1. Photoelectron spectra of B 1s from boron thin film at various temperatures during the deuterium ion irradiation.

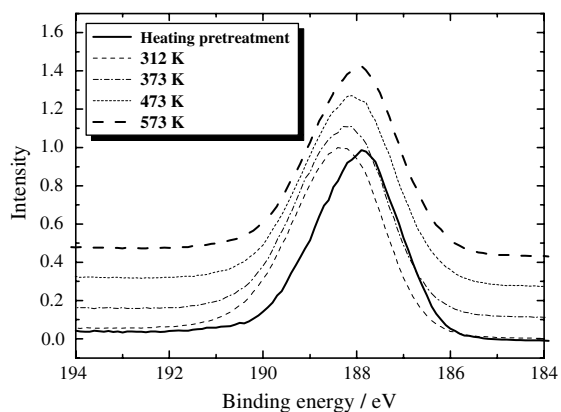


Fig. 2. Photoelectron spectra of B 1s from boron polycrystal at various temperatures during the deuterium ion irradiation.

temperatures during the deuterium ion irradiation. The purities of boron in these boron samples were, respectively, 87% and 96%, by XPS analysis. For the boron thin film in Fig. 1, it was found that the initial B 1s peak position was located at 187.98 eV and its FWHM was 2.09 eV. After deuterium ion irradiation at 312 K, the B 1s peak position was shifted to higher energy, 188.28 eV, and its FWHM was increased to 2.32 eV. These results indicate that the deuterium ion was trapped in the boron thin film and the chemical state of B 1s was changed to a different chemical state in the boron thin film. The B 1s peak, therefore, could be analyzed into two peaks located at 187.98 and 188.28 eV, namely the pure boron state and the B–D bonding state, respectively. On increasing the temperature during the deuterium ion irradiation, the peak position was slightly shifted to lower energy, and a large peak shift was observed between 473 and 573 K, which indicates that the trapped deuterium has started desorbing from the boron thin

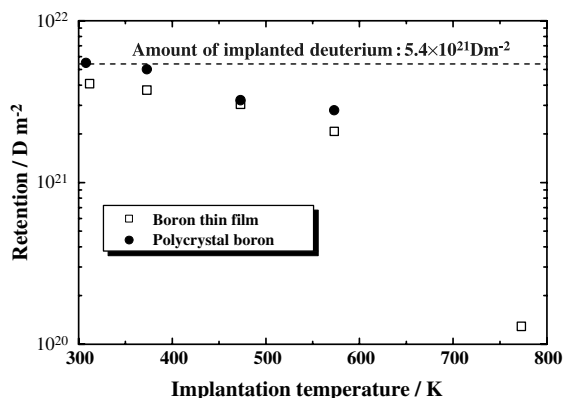


Fig. 3. The deuterium retention in boron at various temperatures during the deuterium ion irradiation.

film. This behavior for the boron thin film was almost the same as that for the boron polycrystal as shown in Fig. 2 and the B 1s peak position was shifted to 188.31 eV after deuterium ion irradiation at 304 K. The large shift was also observed at the same temperature range as for the boron thin film. Total retention at each temperature was estimated by the TDS experimental result and is shown in Fig. 3. It can be seen from this figure that the retention of deuterium at 573 K was decreased less than 35% compared to that for room temperature, and the critical temperature for the hydrogen isotope trapping, when the retention reaches to $1/e$ (0.0625%), was about 700 K. The behavior of hydrogen isotopes in the boron sample was almost the same for these two different samples.

3.2. Estimation of the activation energy by TDS measurement

To understand the detailed B–D interaction and the thermal desorption behavior, TDS experiments were performed with various heating rates. Figs. 4 and 5 show the typical TDS spectra of deuterium obtained from the boron thin film and the polycrystal with heating rates 0.25 to 1.00 K s^{-1} . It can be seen from these figures that a small broad peak was observed at the lower temperature, less than 400 K, and that two clear desorption peaks were found from both of the samples at temperature in the ranges 450–550 and 600–700 K. Since this small broad peak was located at the lower temperature, less than 400 K, it was attributed to the desorption of deuterium adsorbed physically on the surfaces of the samples [12,13]. The activation energies for the two large desorption peaks were estimated by using Redhead equation [10] to be 1.11 ± 0.21 and 2.17 ± 0.36 eV for the boron thin film and 1.36 ± 0.20 and 2.27 ± 0.45 eV for the boron polycrystal, respectively. These activation energies could correspond to the desorption processes

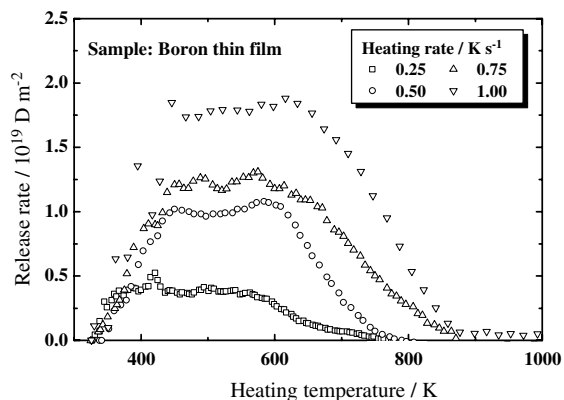


Fig. 4. Thermal desorption spectra of deuterium obtained from boron thin film with various heating rates.

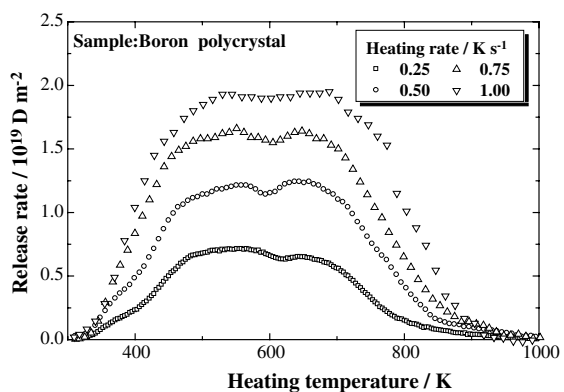


Fig. 5. Thermal desorption spectra of deuterium obtained from boron polycrystal with various heating rates.

for deuterium bound to boron as B–D–B and B–D bonds, respectively [12–14].

The total energy of hydrogen in the boron crystal was determined as a function of B–H bonding distance by the calculation of Gaussian 03 with the model chemistries of HF and B3LYP, and the basic sets of 6–31 + g (d, p) and is shown in Fig. 6. It was found that the total energy of hydrogen in boron was the smallest in the B–H distance of about 1.35 \AA and its activation energy was estimated to be about 0.1 hartree, which corresponds to about 2.7 eV. This result was almost consistent with the experimental values of 2.17 ± 0.36 and 2.27 ± 0.45 eV for the activation energy of deuterium bound to boron as a B–H bond. The distance of B–B bond was about 8 \AA by the optimization. This fact indicates that the B–H–B bond was difficult to form in a perfect boron crystal and would be formed only in the amorphous or polycrystal boron. The B–H–B interaction will be more unstable than B–H interaction because the activation energy was estimated to be about 1 eV and the detailed study by the

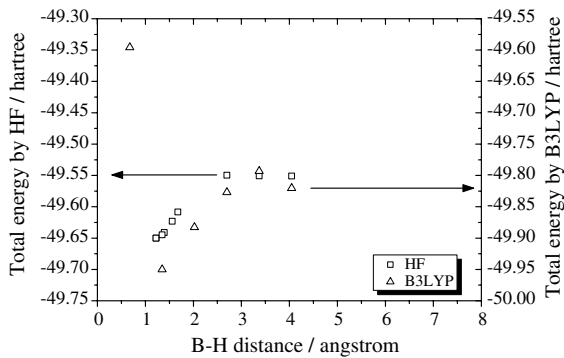


Fig. 6. Energy dependence on B–H distance calculated by Gaussian 03.

calculation will be required to elucidate the boron–hydrogen isotope interaction.

4. Conclusions

Hydrogen isotope behavior in boron polycrystals and thin film were studied by hydrogen isotope implanted into boron and the B–D bond interactions were studied by XPS and TDS. It was found that the retention of deuterium at 573 K was decreased less than 35% compared to that for room temperature and B–B bond was the dominant chemical state in this temperature range by XPS. The critical temperature for the hydrogen trapping, which means the retention reaches to 1/e (0.0625%) compared to that in room temperature, was about 700 K. TDS analysis found that the chemical states of deuterium in boron consists of three parts, namely physical adsorbed deuterium, deuterium bound to boron as B–D–B, and B–D bonds. By Redhead equation, the activation energy of deuterium bound to boron was estimated to be 1.11 ± 0.21 and 2.17 ± 0.36 eV for boron thin film and 1.36 ± 0.20 and 2.27 ± 0.45 eV for boron polycrystal, respectively. The total energy of hydrogen in boron as a function of B–H bonding distance was determined using Gaussian 03 code. It was found that the activation energy of hydrogen in boron was estimated to be about 2.7 eV at the B–H distance of

about 1.35 Å. This result was almost consistent with the experimental results.

Acknowledgements

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