Impurity Effects of Hydrogen Isotope Retention on Boronized Wall in LHD

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Abstract. The impurity effect on hydrogen isotopes retention in the boron film deposited in LHD was evaluated by means of XPS and TDS. It was found that the impurity concentrations in boron film were increased after H-H main plasma exposure in LHD. The ratio of hydrogen retention trapped by impurity to total hydrogen retention during H-H main plasma exposure was reached to 70%, although that of deuterium retention by impurity in D_2^+ implanted LHD-boron film was about 35%. In addition, the dynamic chemical sputtering of hydrogen isotopes with impurity as the form of water and / or hydrocarbons was occurred by energetic hydrogen isotopes irradiation. It was expected that the enhancement of impurity concentration during plasma exposure in LHD would induce the dynamic formation of volatile molecules and their re-emission to plasma. These facts would prevent stable plasma operation in LHD, concluding that the dynamic impurity behavior in boron film during plasma exposure is one of key issues for the steady-state plasma operation in LHD.

1. Introduction

For steady state operations of plasma in fusion devices, it is important to keep the impurities low in vacuum vessels. In the Large Helical Device (LHD) of National Institute for Fusion Science (NIFS), boronization has been applied as a first wall conditioning technique due to quick reduction of impurities such as oxygen and carbon in vacuum vessels [1, 2]. In boronization, boron is deposited on the first wall with the impurities and it is expected that energetic hydrogen isotopes escaped from plasma will implant into the boron film. Therefore, the hydrogen isotopes will interact not only with boron but also with impurities in the boron film, inducing the trapping in film or the release of hydrogen isotopes with water forms, so on. For the evaluation of tritium inventory and fuel recycling behaviors in fusion reactor, the interactions of energetic hydrogen isotopes with the boron film contained with impurities should be elucidated.

In our previous studies, the retention behaviors of energetic deuterium implanted into pure boron films were investigated, and it was found that the energetic deuterium was trapped as B-D-B bridge bond and B-D terminal bond[3]. In addition, for the boron films contained with oxygen, the additional desorption stage of deuterium trapped as B-O-D bond was observed [4]. In the case of the carbon contained boron film, the desorption of deuterium by B-C-D bond was also found [5]. These additional bonds will be formed through the non-equilibrium processes and decomposed in higher temperature compared to the operation temperature. It was also found that deuterium would be quickly released from boron film with impurities by forming heavy water (D_2O) and / or hydrocarbons (CD_x)[4,5]. These volatile species would be introduced into plasma, preventing the stable plasma operation. These facts indicate that the evaluations of the impurity effects on deuterium retention are one of critical issues for the utilization of boronization.

In this study, the energetic deuterium was implanted into LHD-boron film and the chemical state of boron was investigated by means of X-ray photoelectron spectroscopy (XPS) and the

deuterium retention was evaluated by Thermal Desorption Spectroscopy (TDS) for the evaluation of the retention behavior of hydrogen isotopes and the chemical states of boron films deposited in LHD (LHD-boron film). The obtained results were compared to non- and mono- impurity contained boron films with various impurity concentrations deposited by Plasma-assisted Chemical Vapor Deposition (P-CVD). Finally, the behaviors of retention and chemical states for the boron film exposed H-H main discharge in LHD were compared and discussed for the evaluation of hydrogen isotope behaviors for D-D discharge experiment in LHD.

2. Experimental

The LHD-boron film was prepared on the Si substrate in LHD. At first, the Si substrate was exposed to He glow discharge to remove the impurities adsorbed on the substrate surface. Boronization was performed by the glow discharge at 373 K for about 7 hours and the thickness of the boron flim was estimated to be around 50 nm by the combination usage of XPS and Ar^+ sputtering techniques. The diborane (B_2H_6) and He gases were used as material gas and dilute gas, respectively. Thereafter, the sample was introduced to XPS-TDS system at Shizuoka University. The details were found in our previous report [6]. After preheating at 1200 K for 10 min to remove the impurities adsorbed on the surface of boron film, the chemical composition for the LHD boron film was measured by XPS (X-ray Photoelectron Spectroscopy, ULVAC-PHI Inc., ESCA 1600 Series) and found to be 75% for boron, 15% for carbon and 7% for oxygen.

For the comparison of retention behaviors for the LHD-boron film, boron films with impurities were prepared on the Si substrates by the P-CVD apparatus at Shizuoka University [7]. Before the deposition, He plasma exposure was performed for 30 min to clean the sample surface. The decaborane ($B_{10}H_{14}$) gas diluted by He gas was introduced to the P-CVD chamber as the material gases. In addition, oxygen or methane gas was also added as an impurity source gas. The glow discharge was done for 1 h. The thickness of the boron film was estimated to be 150 nm by quartz oscillator. The substrate temperature was kept to be 373 K during the P-CVD process, which is the same as the LHD sample preparation. The chemical composition for the deposited boron films were measured by XPS via the same processed for the LHD-boron film mentioned above.

After the characterizations, D_2^+ was implanted into the boron films at room temperature with the ion energy of 1.0 keV and the flux of 1.0×10^{18} D^+ m^{-2} s^{-1} up to the fluence of 1.0×10^{22} D^+ m^{-2}. After D_2^+ implantation, XPS measurement was carried out to evaluate the trapping state for deuterium. The TDS analysis was also performed from room temperature to 1000 K with the heating rate of 0.5 K / s. The molecules desorbed from the samples were measured by a quadrupole mass spectrometer (QMS).

3. Results and discussion

The D_2 TDS spectra for pure and LHD-boron films are shown in Fig. 1. For pure boron film, it was found that the TDS spectrum was extended from 400 K up to 900 K and consisted of two desorption stages at 500 K and 700 K, namely the desorption of deuterium bound to boron as B-D-B and B-D bonds [8]. In the D_2 TDS spectrum for the LHD-boron film, the additional deuterium desorption stage was observed in the temperature range of 800-1100 K. This desorption temperature corresponded to the temperature of deuterium trapped by carbon and oxygen as C-D and O-D bonds for carbide and oxide materials. These facts indicate these

additional desorption stages were assigned as the desorption of deuterium trapped as B-O-D and B-C-D bonds [9]. These deuterium trapping sites were thermally stable and it would be hardly desorbed during plasma operation, leading that high tritium inventory in boron film. It was also clearly shown that deuterium retention for the LHD-boron film was lower than that for pure boron film. Fig. 2 summarizes the deuterium retentions for various boron films with various impurity concentrations prepared by P-CVD. The deuterium retention for LHD-boron film is also included in this figure. The deuterium retention for the LHD-boron film was less than half compared to that for the pure boron film. It was obvious that the deuterium retention was further low for the boron films with higher impurity concentration shown in Fig. 2, indicating that the impurities contained in boron films induce the chemical sputtering of hydrogen isotopes as heavy water and / or hydrocarbons, which lead the low deuterium retention in boron film. It was also seen that the effect of oxygen on the decreasing of deuterium retention was higher than that of carbon.

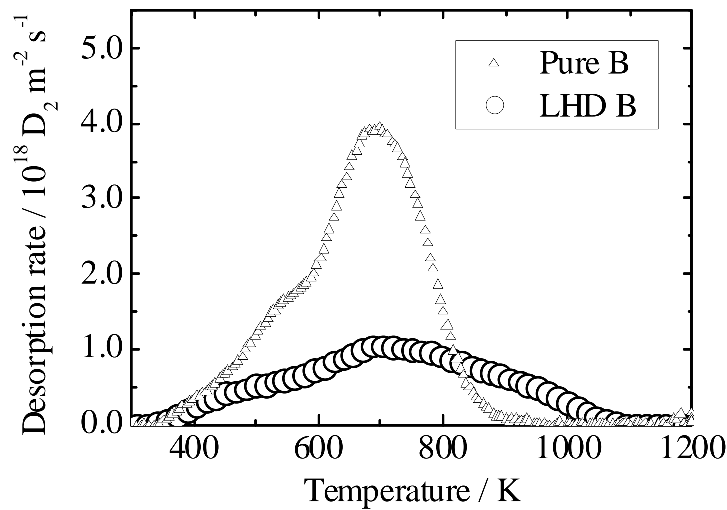

Fig. 1 The D_2 TDS spectra for D_2^+ implanted pure boron film and LHD-boron film.

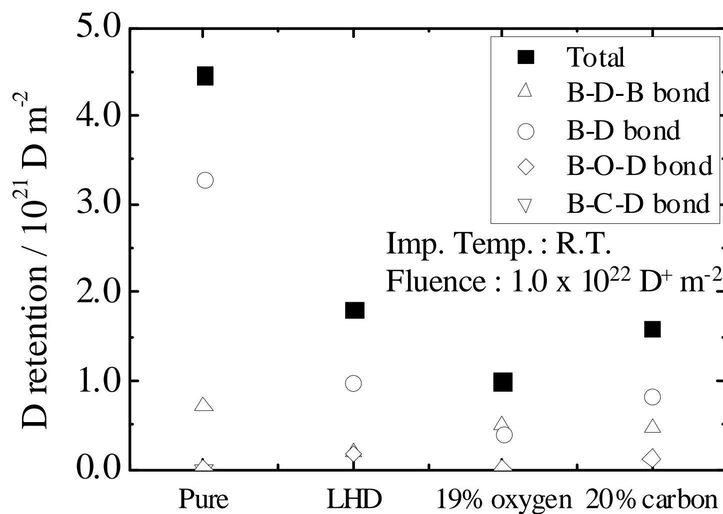

Fig. 2 The Deuterium retentions in D_2^+ implanted various boron films.

For the understanding of dynamic hydrogen isotope retention behavior in boron film during plasma operation in LHD, the hydrogen retention ratio for B-H-B, B-H, B-O-H, B-C-H bonds to total hydrogen retention in LHD-boron film exposed to H-H main plasma discharge in LHD were shown in Fig. 3. In addition, the deuterium retentions for the D_2^+ implanted LHD-boron film mentioned in Fig. 2 were also shown to elucidate hydrogen isotopes trapping process during plasma operation in LHD. As mentioned in Fig. 2, the major deuterium desorption state was B-D bond for the D_2^+ implanted LHD-boron film. On the other hand, that in H-H plasma exposed LHD-boron film was B-O-H bond. The retention ratio as B-C-H bond also increased for this film compared to D_2^+ implanted one. The ratios of deuterium retention as B-O-H and B-C-H bonds, namely hydrogen isotopes trapping by impurities, were reached up to 65% to total hydrogen retention for the LHD-boron film by H-H main plasma exposure, although those for the D_2^+ implanted LHD-boron film were about 35%, indicating that the impurity concentration during the plasma exposure or ion implantation would have a large impact on the retention. Since the atomic concentrations of impurities were increased after H-H plasma exposure, it was considered that the impurities in plasma were introduced to boron film during plasma discharge. This result was consisted with the increase of hydrogen retention ratio as B-O-H and B-C-H in H-H plasma exposed LHD-boron film. The hydrogen isotopes trapping by impurities would be released in higher temperature than operation temperature in LHD, therefore it would be difficult to reduce the hydrogen isotope retention in boron film.

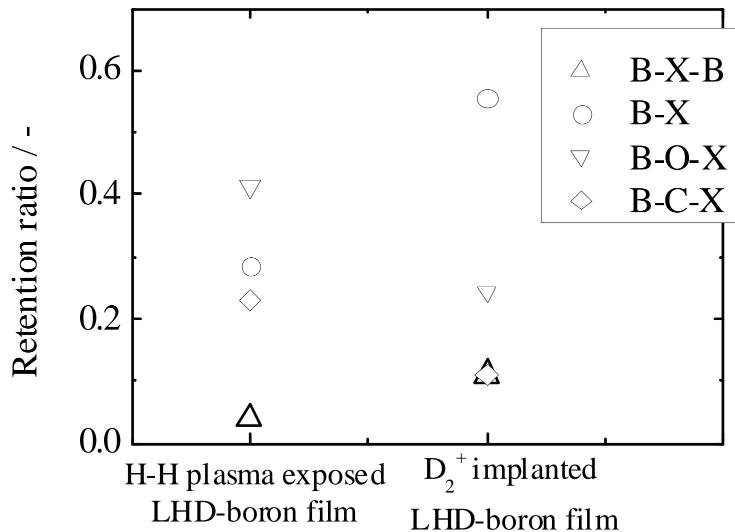

Fig. 3 The hydrogen isotopes retention ratio as each desorption peak in H-H main plasma exposed and D_2^+ implanted LHD-boron film. (X means hydrogen isotopes)

In the D_2^+ implanted LHD boron film, the deuterium retention was low compared to that in pure boron film as shown in Fig. 1. In addition, as the impurity concentration increased, the deuterium retention decreased for oxygen or carbon contained boron films as mentioned in Fig. 2, indicating the chemical sputtering of deuterium has a large impact on deuterium retention. In the O-1s XPS spectrum for the LHD-boron film before D_2^+ implantation, it was found that the major chemical states of oxygen were B-O bond and free oxygen which is interstitial oxygen in the boron film[10], which is almost the same as C-1s XPS result, where the main chemical states were B-C bond and free carbon[11]. In our previous studies, the chemical states of B-O and B-C bonds were associated with the formation of B-O-D and B-C-

D bonds, respectively [4, 5]. The peak area for each chemical state of oxygen was shown in Fig. 4. After D_2^+ implantation, the peak area for free oxygen was clearly decreased although that for B-O bond showed little change. Similar behavior was observed for the C-1s XPS spectra for LHD-boron film. It was considered that energetic deuterium would react with oxygen or carbon, especially free oxygen or free carbon, and form the heavy water or hydrocarbons, respectively. These volatile molecules would be easily released to vacuum vessel during implantation which is almost consistent with the experimental fact that the large amount of M/e=20 (D_2O and/or CD_4) was desorbed in implantation process.

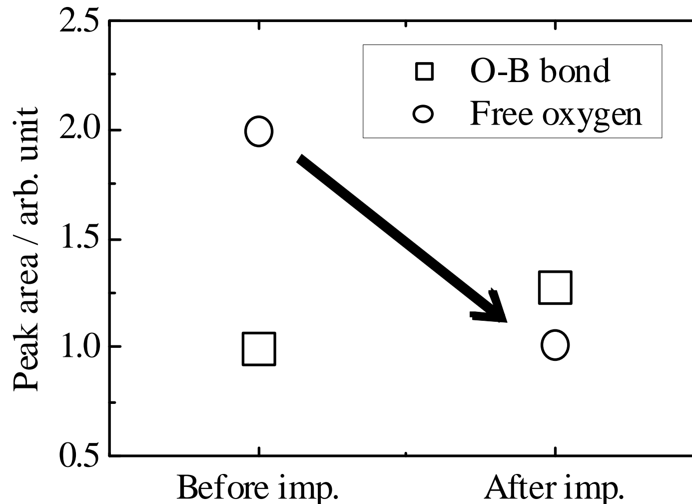

Fig. 4 The peak area changes for B-O bond and free oxygen before and after D_2^+ implantation into LHD-boron film.

As mentioned above, the increase of impurity concentration for boron film was found by H-H plasma exposure in LHD, concluding that the retention and sputtering of hydrogen isotopes by impurities in boron film would be correlated with the chemical states of impurity. Furthermore, impurities will be introduced into boron film by plasma operation in fusion devises, leading the increase of the retention ratio of hydrogen isotopes trapped by impurity and the amount of sputtered molecules into the plasma. These facts would be a critical issue for the evaluation of dynamic hydrogen isotopes recycling in fusion devices.

4. Conclusions

In this study, the impurity effect on hydrogen isotopes retention in the boron film deposited in LHD was evaluated be means of XPS and TDS. It was found that the impurity concentrations in boron film increased after H-H main plasma exposure in LHD. The ratio of hydrogen retention trapped by impurity to total hydrogen retention for LHD-boron film was reached to 65%, although that for the D_2^+ implanted LHD-boron film was about 35%. In addition, the dynamic chemical sputtering by energetic hydrogen isotopes induce the formation of water and / or hydrocarbons. It was expected that the enhancement of impurity concentration during plasma exposure in LHD would lead the dynamic formation of volatile molecules and the re-emission of these to plasma. These facts would prevent the stable

plasma operation, therefore the dynamic impurity behavior in boron film during plasma exposure is a key issue for the steady-state plasma operation in LHD.

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