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Chemical behavior of hydrogen isotopes into boronized film in LHD

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ABSTRACT

In D-T fusion experimental devices, it is expected that oxygen and carbon could be contained as impurities in boron film produced by boronization. The chemical behavior of hydrogen isotopes implanted into boron films prepared in LHD at NIFS was studied by comparing the LHD sample with the P-CVD samples prepared at Shizuoka University. The LHD sample formed B–D–B, B–D, B–C–D and B–O–D bonds by D_2^+ implantation. B–C–D and B–O–D bonds were mainly formed by the reaction of B–C and B–O bond with implanted D_2^+, and C–C bond and free oxygen were mainly formed the hydrocarbon and water during D_2^+ implantation. It was suggested that the total D retention of the LHD sample was slightly larger than that of only the carbon- or oxygen-containing boron sample prepared by P-CVD. This could be largely affected to the amount of C–C bond and free oxygen which formed the hydrocarbon and water.

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1. Introduction

Boronization as one of the first wall conditioning techniques has been applied to many fusion devices such as JT-60U of JAEA (Japan Atomic Energy Agency) and LHD (Large Helical Device) of NIFS (National Institute for Fusion Science) [1–4]. Present key issues are however the sputtering and/or production of boron as impurity by particles and neutron from the plasma. During the boronization, it is well known that the boron is easily bound with various impurities such as oxygen and carbon, and helps to keep a low impurity concentration in the plasma [4–7]. It is thought that hydrogen isotopes, such as tritium and deuterium will be implanted into the impurities-containing boron film during D-T discharge. Therefore, the elucidation of chemical behavior of tritium implanted into the boron film which deposited under fusion circumstance is one of the most important issues for the evaluation of fusion safety.

In our previous studies, the hydrogen isotope behavior in the pure boron film, oxygen-containing boron film and carbon-containing boron film were studied, and it was found that the implanted D_2^+ was trapped in the boron film with forming B–D–B, B–D and B–O–D or B–C–D bonds by containing the impurities, although only B–D–B and B–D bonds were appeared for the pure boron film [8–12]. It was reported that the total D retention in the oxygen-containing boron film was decreased to a quarter compared to that of pure boron [10]. In this study, it was focused on the chemical behavior of hydrogen isotopes implanted into boron film prepared in LHD. Pure, oxygen-containing and carbon-containing boron films were also prepared by P-CVD apparatus, and used in this study to compare that of LHD one.

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2. Experiments

2.1. The preparation of the LHD sample

The LHD sample was prepared on the Si substrate, in 10th discharge campaign in LHD at NIFS. The Si substrate was firstly exposed the He glow discharge to remove the impurities such as hydrogen and water on the substrate surface. Boronization was performed by the glow discharge at 373 K for about 7 h, and the thickness of the sample was estimated to be around 50 nm by depth profiling. Diborane (B_2H_6) and He gases were used as material gas and dilute gas, respectively. The chemical composition of LHD boron film was estimated by XPS (X-ray Photoelectron Spectroscopy, ALVAC-PHI Inc., ESCA 1600 Series) to be 75% for boron, 15% for carbon and 7% for oxygen.

2.2. The preparation of P-CVD samples

The carbon- or oxygen-containing boron film was prepared on the Si substrates by the plasma CVD (P-CVD) apparatus at Shizuoka University. Before the deposition, the He plasma was performed for 30 min to clean the sample surface. Thereafter, decaborane ($B_{10}H_{14}$) and 5% oxygen or methane gases diluted by helium gas were introduced and the glow discharge was done for 1 h. The thickness was estimated to be 150 nm by quartz oscillator. The

substrate temperature was kept to be 373 K during the deposition process, which is the same as the LHD sample preparation. The atomic composition was evaluated to be 75% boron, 4% carbon and 19% oxygen for the oxygen-containing boron film namely Sample A, and 70% boron, 22% carbon and 5% oxygen for the carbon-containing boron film, named as Sample B, respectively.

2.3. XPS and TDS measurements

For all samples, after heating at 1200 K for 10 min as a pretreatment, the deuterium ion (D_2^+) was implanted into the samples for 7300 s with an ion energy of 1.0 keV and an ion flux of 1.0×10^{18} D^+ m^{-2} s^{-1}. Implantation depth of 1.0 keV D_2^+ was estimated to be 10–20 nm for each sample by SRIM codes. After the D_2^+ implantation, XPS measurements and TDS (Thermal Desorption Spectroscopy) were carried out. It was found from B-1s, O-1s and C-1s XPS spectra in both samples that no probability of perturbation effects with insulating was caused. The heating rate for TDS was set to be 0.5 K s^{-1} and all samples were heated up from the room temperature to 1200 K. The molecules (mainly $m/e = 4$ and 20) desorbed from the samples were measured using a quadrupole mass spectrometer (QMS).

3. Results and discussion

Fig. 1 shows the B-1s XPS spectra for all samples (a) before and (b) after the D_2^+ implantation. It was estimated from the peak separation of B-1s XPS spectra that the peaks for the B–B, B–C and B–O bonds were located at around 188, 189 and 190 eV for the LHD sample [11,12]. Only B–B and B–O bonds were observed in Sample A, and only B–B and B–C bonds were also formed in Sample B. From Fig. 1(b), it was found that the peak energies of B-1s XPS spectra for all samples were shifted toward higher energy side by D_2^+ implantation, indicating that boron, carbon and/or oxygen were bound to D [10–12]. Fig. 2 shows the peak separation for C-1s XPS spectrum for the LHD sample. It was clear that C-1s XPS spectrum in the LHD sample consisted of two types of chemical states, namely B–C bond contributed to the structure of $B_{11}C$ and C–C bonds, which were

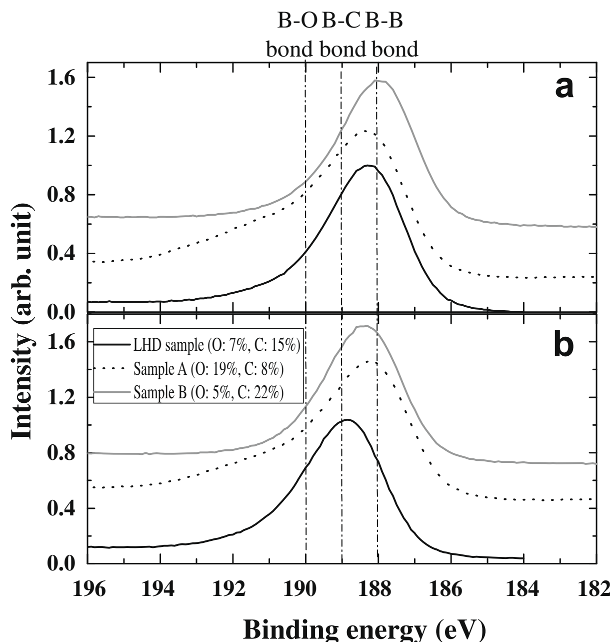

Fig. 1. The B-1s XPS spectra for each sample (a) before and (b) after D_2^+ implantation.

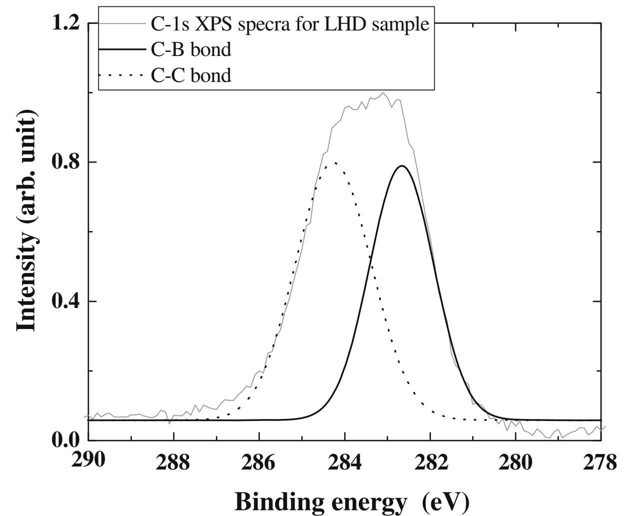

Fig. 2. The result of the peak separation of C-1s XPS spectra for the LHD sample.

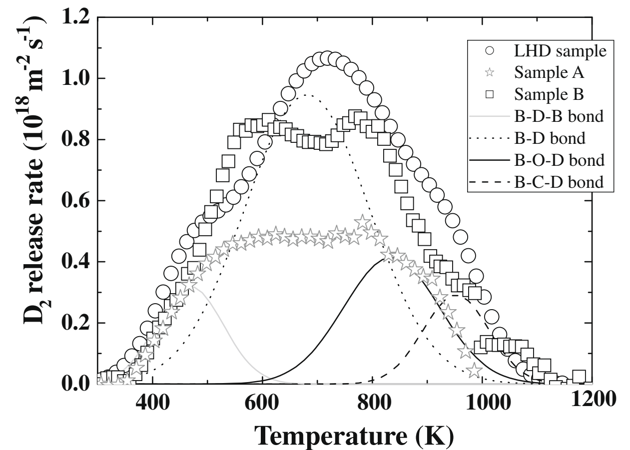

Fig. 3. TDS spectra of D_2 for each sample.

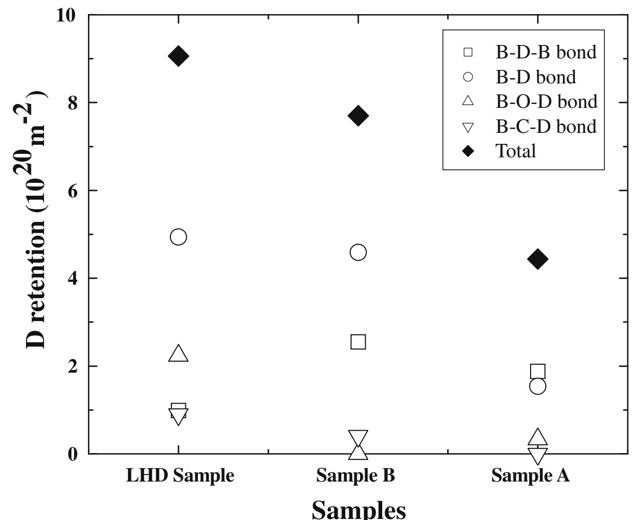

Fig. 4. The deuterium retentions of total and each peak.

Table 1
The peak area ratios of C–B and C–C bonds from the C-1s XPS spectra and O–B bond and free oxygen from the O-1s XPS spectra.

	(a) C-ls XPS results				(b) O-1s XPS results			
	The peak area ratios of C–B bond	The peak area ratios of C–C bond	Peak shift of C–B bond (eV)	Peak shift of C–C bond (eV)	The peak area ratios of O–B bond	The peak area ratios of free oxygen	Peak shift of O–B bond (eV)	Peak shift of free oxygen (eV)
LHD sample	1.05	0.79	0.5	0.2	1.28	0.61	0.6	0.3
Sample A	–	–	–	–	1.09	0.34	0.7	0
Sample B	0.63	0.15	0.6	0	–	–	–	–

located at the peak energies of around 283.0 and 284.5 eV, respectively [13]. It was found from O-1s XPS spectra of the LHD sample and Sample A before D_2^+ implantation, free oxygen and O–B bond were formed, which peak energies were placed at around 532.3 and 533.2 eV [14,15].

The D_2 TDS spectra and peak analysis using Gaussian distribution function for all samples were shown in Fig. 3. It was found from the peak analysis of each D_2 TDS spectrum that the B–D–B, B–D, B–O–D and B–C–D bonds were formed in the LHD sample, and these desorption temperatures were located to be around 450 K for B–D–B bond, 700 K for B–D bond, 850 K for B–O–D bond and 950 K for B–C–D bond, the desorption stages of D as B–D–B, B–D and B–O–D bonds were found for Sample A, and B–D–B, B–D and B–C–D bonds for Sample B, respectively [8–12].

Fig. 4 summarizes the total D retention and the amount of D trapped by each trapping site. Total D retention for the LHD sample was larger than those for Sample A and Sample B. The D retention bound to B with forming B–D bond, governed total D retention in all samples. The amount of D trapped as B–O–D and B–C–D bonds in the LHD sample were also almost the same as that of B–O–D bond as Sample A and that of B–C–D bond as Sample B. This result was indicated that the retentions of D as B–C–D and B–O–D bonds were almost constant regardless of carbon or oxygen concentration for all samples.

Table 1(a) summarizes the peak area ratios of C–B and C–C bonds for the LHD sample and Sample B between before and after the D_2^+ implantation, namely the peak area of C–B bond or C–C bond for the LHD sample and Sample B after D_2^+ implantation to that before D_2^+ implantation. The ratio of peak area for C–B bond for the LHD sample was almost unit, although that for C–C bond was reached less than 0.8, indicating that the C–C bond was dissociated by D_2^+ implantation. This trend was also found for Sample B. In addition, the peak position for C–B bond in the LHD sample and Sample B was shifted to higher energy side by D_2^+ implantation around 0.5 and 0.6 eV, respectively, although the peak energy of C–C bond was almost constant. This indicates that the D bound to C–B bond was trapped by B with forming B–C–D bond and C–C bond would be dissociated with D with forming hydrocarbon by the chemical sputtering during the D_2^+ implantation, which was consistent with the TDS result as mentioned above. Table 1(b) also summarized the peak area ratios of O–B bond and free oxygen for the LHD sample and Sample B before and after D_2^+ implantation and their peak shifts. It was also found that the area ratio of O–B bond was almost unity. The ratio of free oxygen was, however, largely decreased by D_2^+ implantation for both samples. The large positive peak shifts of 0.6 and 0.7 eV for O–B bond in the LHD sample and Sample A were found, respectively, although no peak shift of free oxygen was derived. These results suggested that D would be trapped by B with forming B–O–D in the boron film, and the D bound to free oxygen was thought to be released as D_2O during the D_2^+ implantation. It can be said that the formation of hydrocarbon or D_2O made a role of the reduction of the D retention in the boron film.

It was anticipated that the boron film prepared at LHD is contained around 10–20% of impurities, namely carbon and oxygen. The tendency was also consistent with that for the boron film prepared at JT-60U [7]. It was indicated in this study that the total retention of hydrogen isotopes is governed by the chemical states of impurities in boron film. If the concentrations of impurities, however, increase, it was suggested that the total hydrogen isotopes retention decreases because of the C–C bond or free oxygen would be major chemical state and easily react with hydrogen isotopes. C–C bond and free oxygen would be detrapped quickly with forming hydrocarbon and/or water molecules. These molecules might be contaminated with the D-T plasma, although total retention of hydrogen isotopes in boron film would be decreased, and this result might be one of the key issues from the view point of tritium safety.

4. Conclusion

The chemical behavior of deuterium implanted into boron film which boronized at real fusion experimental were estimated using XPS and TDS by comparing the chemical composition of boron films boronized at LHD of NIFS and Shizuoka University. From the XPS measurements, B–B, B–C, B–O, C–C bonds and free oxygen were formed in the film boronized at LHD. From the TDS measurements, B–D–B, B–D, B–C–D and B–O–D bonds were also formed by D_2^+ implantation in the LHD sample. It was suggested from the XPS and TDS measurements that D bound to the B–C and B–O bonds were trapped with forming B–C–D and B–O–D bonds, and D bound to C–C bond and free oxygen were released by chemical sputtering during the D_2^+ implantation with forming D_2O and hydrocarbon. The total D retention in the LHD sample was slightly increased compared to that of only oxygen- or carbon-containing boron film as the B–C–D and B–O–D bonds were formed in the LHD sample. If the concentrations of impurities, however, increase, it was suggested that the total hydrogen isotopes retention decreases because of the C–C bond or free oxygen would be major chemical state and easily react with hydrogen isotopes. C–C bond and free oxygen would be detrapped quickly with forming hydrocarbon and/or water molecules. These molecules might be contaminated with the D-T plasma, although total retention of hydrogen isotopes in boron film would be decreased, and this result might be one of the key issues from the view point of tritium safety.

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