

## **Retention Behavior of Hydrogen Isotopes in Boron Film Deposited on SS-316 for LHD first wall**

Kenji Okuno<sup>1</sup>, Sachiko Suzuki<sup>1</sup>, Makoto Kobayashi<sup>1</sup>, Rie Kurata<sup>1</sup>,  
Matsuyama Masao<sup>2</sup>, Naoko Ashikawa<sup>3</sup>, Akio Sagara<sup>3</sup> and Yasuhisa Oya<sup>1</sup>

<sup>1</sup>Radioscience Research Laboratory, Faculty of Science, Shizuoka University, Shizuoka,  
422-8529 Japan

<sup>2</sup>Hydrogen Isotope Research Center, University of Toyama, Toyama, Japan

<sup>3</sup>National Institute for Fusion Science, Gifu, Japan

[Corresponding Author]

Name : Kenji Okuno

Postal address : Radioscience Research Laboratory, Faculty of Science, Shizuoka University, 836

Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Telephone number : +81-54-238-4802

Fax number : +81-54-238-3989

E-mail address : [srkokun@ipc.shizuoka.ac.jp](mailto:srkokun@ipc.shizuoka.ac.jp)

Total pages : 14

Figures: 5

Tables: 0

Keyword: boronization, LHD, SS316, XPS, TDS

## **Abstract**

The chemical states and the deuterium retention of boron films deposited on type 316 stainless steel used as first wall of LHD, which contained 52 % oxygen, were studied by means of XPS and TDS. The high oxygen concentration in the boron film could be attributed to oxygen in the surface oxide layer of the stainless steel. The major chemical state of boron with 52 % oxygen concentration was  $B_2O_3$ . The  $B_2O_3$  structure was decomposed to B-B and B-O bonds by the energetic deuterium irradiation. It was found that the deuterium could remain in boron films under operation temperature in the first wall of LHD. The deuterium retention in the boron film deposited on SS was smaller compared to that in the boron film deposited on silicon substrate with 36% oxygen concentration. As the oxygen concentration in boron films increased, the amount of sputtered oxygen was clearly increased, indicating that more heavy water was formed by reacting with implanted deuterium and released, resulting in the smaller deuterium retention in the boron films. The knowledge for the tritium retention in boron films which cannot remove in the operation temperature and the release of tritiated water should be required for the D-D discharge in LHD.

## Introduction

For steady state operations of D-T 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[1]. Boron easily bounds to the impurities such as oxygen and carbon existing in vacuum vessels [2]. In boronization, boron is deposited on the first wall with the impurities and it is expected that energetic hydrogen isotopes including tritium escaped from D-T plasma will implant into the boron film contained with impurities. The implanted tritium will be trapped not only by boron but also by impurities in the boron film. Therefore, for the evaluation of tritium inventory in fusion reactor, the interactions of the 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 revealed 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 peak of B-O-D bond was appeared [4], and for the boron films contained with carbon, B-C-D bond was formed [5]. These additional bonds were formed through the non-equilibrium processes and decomposed in higher temperature than the operation temperature during the plasma discharge. It was also found that the deuterium was easily trapped by impurities than by boron, although the deuterium retention in the boron films decreased as the concentration of impurities increased, indicating that the implanted deuterium would be quickly released from boron film with impurities by forming heavy water ( $D_2O$ ) or hydrocarbons

(CD<sub>x</sub>)[4,5]. These volatile species would be introduced into D-T plasma, preventing the D-T plasma stable. These facts indicate that the evaluations of the impurity effects on deuterium retention are one of critical issues for boronization.

The type 316 stainless steels (SS) will be widely used in various components in fusion devices. Especially, in LHD, SS are used as a first wall material. It is well known that the oxide layer is quickly formed on the surface of SS [7]. It is expected that the oxygen in oxide layer would be introduced in boron films during the deposition, leading the formation of boron films contained with oxygen. In this study, the chemical states of boron films deposited on SS were elucidated by means of X-ray photoelectron spectroscopy (XPS). The retention behaviors of deuterium which should correlate with the chemical states of boron films were also investigated by Thermal Desorption Spectroscopy (TDS). The obtained results were compared with those in boron films deposited on silicon substrate.

## **Experimental**

In this study, three types of boron films were prepared in different condition. Two of them were prepared as follows; the type 316 SS and the silicon were introduced into P-CVD (Plasma-chemical vapor deposition) chamber at the same time. The atomic concentration of oxygen on the SS surface was 40 %. The boron films were deposited on the SS and the silicon substrates at room temperature with the flowing rates of the 2.5 sccm of decaborane (C<sub>10</sub>H<sub>14</sub>) gas as the material gases, and the 3.8 sccm of helium gas as the dilute gas. During the operation, the pressure in vacuum vessel was kept at 25 Pa. The impurity source gas was not introduced into P-CVD.

For the comparison to the boron film prepared above, an oxygen contained boron film

was deposited on silicon substrate as follows; the silicon substrate was introduced into P-CVD chamber and boronization was performed at room temperature with the same flowing rates of  $B_{10}H_{14}$  and He as mentioned above. In this process, 2.0 sccm of oxygen gas was also introduced as the oxygen impurity source gas. After P-CVD operation, the boron film with 36 % oxygen concentration was formed on silicon substrate.

After the deposition, the atomic composition and chemical states of the samples were evaluated by XPS (ESCA 1600 Series, ULVAC PHI Inc.). The depth profiles were also done by the combination usage of XPS and  $Ar^+$  sputtering technique. After the characterizations,  $D_2^+$  was implanted into the samples at room temperature with the ion energy of 1.0 keV and the flux of  $1.0 \times 10^{18} D^+ m^{-2} s^{-1}$  up to the fluence of  $1.0 \times 10^{22} D^+ m^{-2}$ . After  $D_2^+$  implantation, XPS measurement was carried out to evaluate the change of chemical state by the deuterium implantation. 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 sample were measured by a quadrupole mass spectrometer (QMS).

## **Results and Discussion**

The atomic concentrations of boron and oxygen in the boron film deposited on SS substrate (B on SS) were 43 % and 52 %, respectively. Those of carbon and nitrogen were less than 5 %. Figure 1 shows the B-1s XPS spectra as a function of the depth in B on SS. Those for the boron film on silicon substrate deposited together with B on SS were also shown in this figure. It was considered that boron existed with forming some chemical states, B-B bond corresponding to boron network (187.8 eV), B-O bond (192.0 eV) and  $B_2O_3$  (193.2 eV) which was the major chemical state in B on SS [8. 9]. In the case of boron on the silicon substrate deposited together with B on SS, the atomic

concentrations of boron, oxygen and carbon were 75 %, 8 %, 12 %, respectively and the B-B bond was the major chemical state in this film, showing that the lower concentration of oxygen in boron on silicon substrate. It should mean that the higher concentration of oxygen in B on SS would be derived from the SS substrate. It is known that thick oxide layer was formed on the surface of SS and such high concentration of oxygen would be contaminated in the boron film. The depth analysis for B on SS by XPS with using Ar<sup>+</sup> sputtering technique indicated that the peak positions of B-1s were almost fixed, indicating that the formed boron film is uniform toward the depth. Figure 2 represents the D<sub>2</sub> TDS spectrum for B on SS with the oxygen concentration of 52 %, and the results of peak separation analysis using Gaussian distribution function were added. The D<sub>2</sub> TDS spectrum for boron film contained with 36 % oxygen concentration deposited on silicon substrate which was reported in our previous study[4] was also shown. The deuterium was desorbed in the temperature range of 400-1000 K for both samples. However, the deuterium retention was clearly reduced for B on SS compared with that for the boron film contained with 36 % oxygen concentration deposited on silicon substrate. The D<sub>2</sub> TDS spectrum consisted of three stages, B-D-B bridge bond (500 K), B-D terminal bond (630 K) and B-O-D bond (780 K). It was considered that the hydrogen isotopes retained as B-D and B-O-D bonds in B on SS can be remained under the temperature of first wall in LHD. The deuterium retentions as various trapping states in the B on SS and the boron films contained with 36 % oxygen were summarized in Fig. 3. The deuterium retentions as B-D-B bond and B-D bond were quite different among these two samples. Figure 4 shows the B-1s XPS spectra before and after D<sub>2</sub><sup>+</sup> implantation for the B on SS and the boron film contained with 36 % oxygen concentration deposited on silicon substrate. The chemical states of boron in the boron

film contained with 36 % oxygen concentration deposited on silicon substrate were B-B bond, B-O bond and  $B_2O_3$  state. After  $D_2^+$  implantation into B on SS, the peak around 188 eV was appeared. Then, the FWHM of the peak located about 193 eV was broadened. These results would show that the dissociation of  $B_2O_3$  structure to simple B-B bond and B-O bond by the energetic deuterium implantation.

Major chemical state as  $B_2O_3$  for B on SS after the deposition was changed to B-B and B-O bonds indicates that the  $B_2O_3$  structure does not have much affinity with hydrogen isotopes, which induces the deuterium retention low compared to that for the boron film contained with 36 % oxygen concentration deposited on silicon substrate. This fact indicates that the implanted deuterium would be trapped by B-B bond and/or B-O bond. In the O-1s XPS spectra, the peak areas of O-1s XPS spectra for both of the B on SS and the boron film contained with 36 % oxygen concentration deposited on silicon substrate were decreased after the deuterium implantation, although the decreasing peak area for B on SS was three times as large as that for the boron film contained with 36 % oxygen concentration deposited on silicon substrate, proposing that more heavy water was released to vacuum vessel during the implantation for B on SS, which is almost consistent with the experimental fact that the large amount of  $M/e=20$  ( $D_2O$ ) was desorbed for B on SS. Therefore, the re-emission of water would contaminate the plasma and oxygen concentration should be taken into account. For the D-D discharge in LHD, it is expected that the tritium retain in boron film and the release of tritiated water, therefore the removal of oxide layer of SS is important from the view point of the establishment of steady state plasma operations and the tritium safety.

## **Conclusion**

The chemical states and the deuterium retention behavior in the boron film deposited on stainless steel were investigated by means of XPS and TDS. The atomic concentrations of boron and oxygen in the boron film deposited on stainless steel were 43 % and 52 %, respectively. This high concentration of oxygen was derived from oxide layer forming on the surface of stainless steel. Major chemical state of boron with 52 % oxygen concentration deposited on stainless steel was  $B_2O_3$ , which decomposes to the B-B bond, B-O bond by the irradiation of energetic deuterium. The deuterium was retained in boron film deposited on stainless steel as B-D-B, B-D and B-O-D bonds. The oxygen concentrations for the boron films were decreased after the deuterium implantation, which indicates the formation and the release of heavy water during the deuterium implantation, leading the refrain of deuterium retentions. In addition, as oxygen concentration increases, more heavy water would be released and re-introduced to plasma, making the plasma unstable. For safety and steady state operations of D-D discharge in LHD, it was considered that the elimination of the surface layer on the first wall materials before boronization is essential treatment to reduce the release of tritiated water.

### **Acknowledgement**

This study has been supported by the NIFS and the Center for Instrumental Analysis at Shizuoka University.

### **Reference**

[1] A. Sagara, Y. Hasegawa, K. Tsuzuki, N. Inoue, H. Suzuki, T. Morisaki, N. Noda, O. Motojima, S. Okamura, K. Matsuoka, R. Akiyama, K. Ida, H. Idei, K. Iwasaki, S. Kubo,

- T. Minami, S. Morita, K. Narihara, T. Ozaki, K. Sato, J. Nucl. Mater. 241–243 (1997) 972–976.
- [2] B. Lipschultz, Y. Lin, E.S. Marmor, D.G. Whyte, S. Wukitch, I.H. Hutchinson, J. Irby, B. LaBombard, M.L. Reinke, J.L. Terry, G. Wright and The Alcator C-Mod Group, J. Nucl. Mater. 363–365 (2007) 1110–1118.
- [3] M. Oyaidzu, A. Yoshikawa, H. Kodama, Y. Oya, A. Sagara, N. Noda, K. Okuno, Appl. Sur. Sci. 244 (2005) 240–243.
- [4] A. Yoshikawa, M. Oyaidzu, H. Miyauchi, Y. Oya, A. Sagara, N. Noda, K. Okuno, J. Nucl. Mater. 367–370 (2007) 1527–1530.
- [5], S. Suzuki, Y. Yang, A. Yoshikawa, Y. Kikuchi, A. Sagara, Y. Oya, K. Okuno, J. Nucl. Mater. 390–391 (2009) 200–202.
- [6], M. Oyaidzu, A. Yoshikawa, H. Kodama, Y. Oya, A. Sagara, N. Noda, K. Okuno, Appl. Sur. Sci. 244 (2005) 240–243.
- [7] N. Ashikawa, K. Kizu, J. Yagyu, T. Nakahata, Y. Nobuta, K. Nishimura, A. Yoshikawa, Y. Ishimoto, Y. Oya, K. Okuno, N. Miya, T. Hino, S. Masuzaki, A. Sagara, N. Ohyanagi and LHD Experimental Group, J. Nucl. Mater. 363–365 (2007) 1352–1357.
- [8] M.J. Zhou, S.F. Wong, C.W. Ong and Quan Li., *Thin Sol. Films*, 2-4 (2007) 336-339.
- [9] O. M. Moon, B.-C. Kang, S.-B. Lee, J.-H. Boo, *Thin sol. films*, 464-465 (2004) 164-169.

### Figure captions

Fig. 1 The B-1s XPS spectra toward the depth for (a) boron film deposited on SS and (b) boron film deposited on silicon with the same condition.

Fig. 2 The D<sub>2</sub> TDS spectra and the results of peaks separation analysis for (a) the B on SS and (b) the boron film contained 36 % oxygen.

Fig. 3 Retentions of deuterium as B-D-B, B-D and B-C-D bonds for the B on SS and the boron film contained 36 % oxygen.

Fig. 4 The B-1s XPS spectra for two different boron films before and after deuterium implantation.

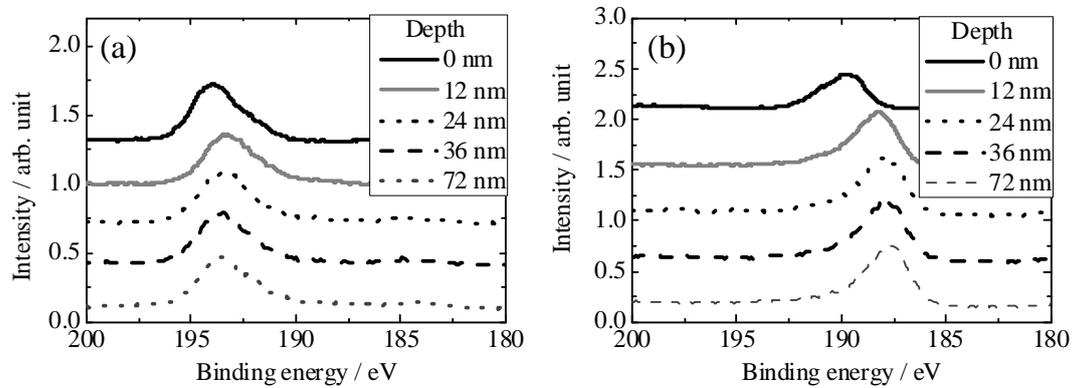


Figure 1 Okuno et al.

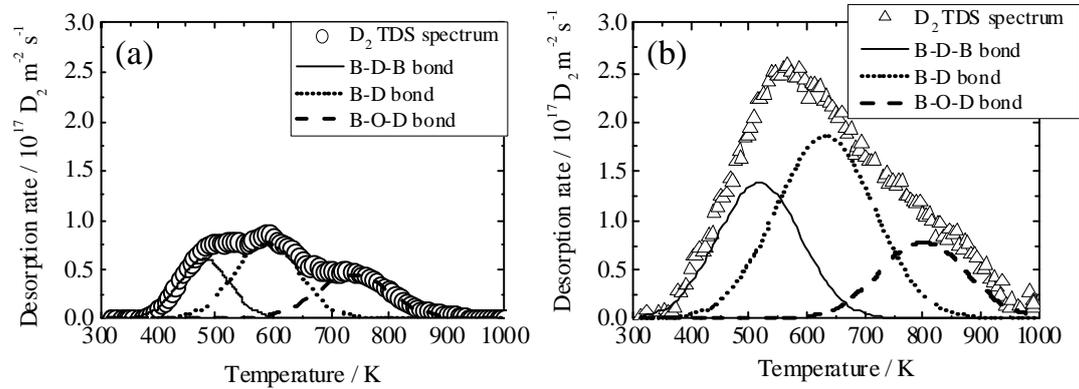


Figure 2 Okuno et al.

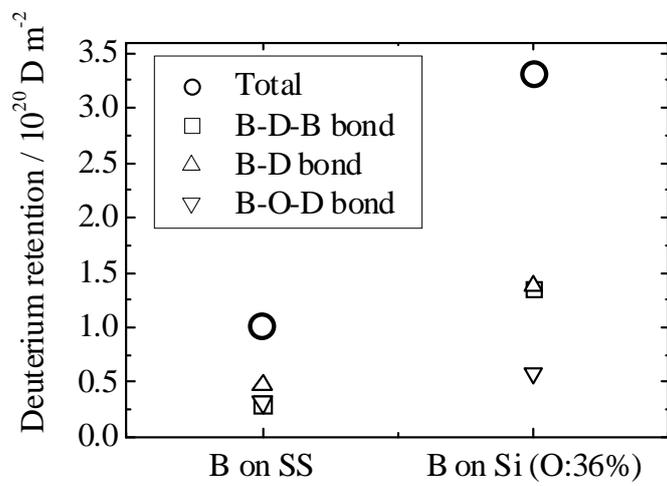


Figure 3 Okuno et al.

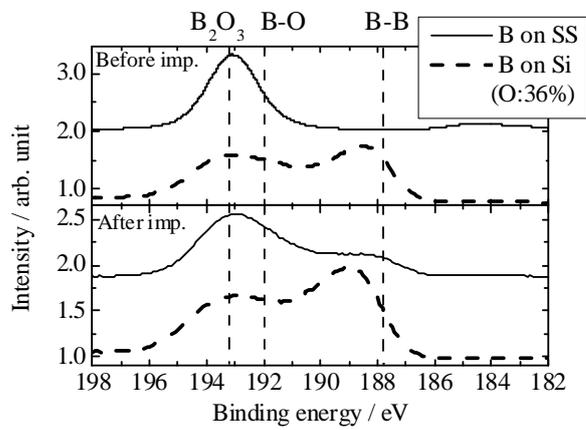


Figure 4 Okuno et al.